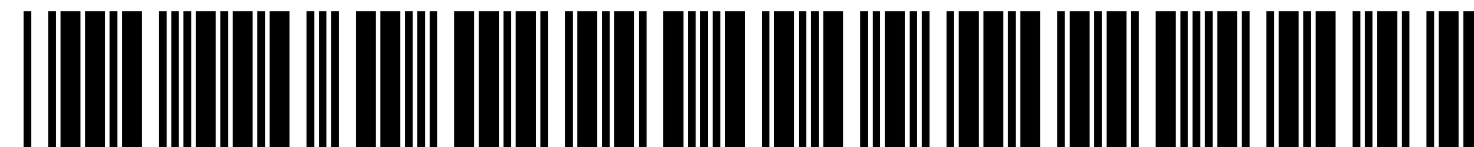
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Sandhu et al.

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(45) **Date of Patent: Nov. 26, 2013**

(54) **MULTILEVEL MIXED VALENCE OXIDE (MVO) MEMORY**

(75) Inventors: **Gurtej S. Sandhu**, Boise, ID (US); **Eugene P. Marsh**, Boise, ID (US)

(73) Assignee: **Micron Technology, Inc.**, Boise, ID (US)

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(52) **U.S. Cl.**
USPC **257/4**; 257/E45.002; 257/E21.09; 438/382

(58) **Field of Classification Search**
None
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,687,112 A 11/1997 Ovshinsky
6,791,102 B2 9/2004 Johnson et al.
7,524,722 B2 4/2009 Lee et al.
7,697,316 B2 4/2010 Lai et al.
8,233,311 B2 * 7/2012 Shimakawa et al. 365/148
8,330,139 B2 12/2012 Ramaswamy et al.
2006/0002174 A1 * 1/2006 Hosoi et al. 365/148
2006/0003489 A1 * 1/2006 Zhang et al. 438/102
2007/0165442 A1 * 7/2007 Hosoi et al. 365/100
2007/0269683 A1 * 11/2007 Chen et al. 428/697
2008/0025072 A1 * 1/2008 Tamai et al. 365/148
2009/0078983 A1 3/2009 Nakasaki et al.
2009/0134432 A1 5/2009 Tabata et al.
2009/0289251 A1 11/2009 Kiyotoshi
2010/0155723 A1 * 6/2010 Bornstein et al. 257/43
2010/0167463 A1 * 7/2010 Sung 438/104
2010/0188884 A1 * 7/2010 Mitani et al. 365/148
2010/0207094 A1 * 8/2010 Kanzawa et al. 257/4
2010/0208508 A1 8/2010 Baek
2011/0068316 A1 3/2011 Takano et al.
2011/0161605 A1 * 6/2011 Lee et al. 711/154
2012/0086104 A1 * 4/2012 Marsh 257/532
2012/0241711 A1 9/2012 Ramaswamy et al.
2013/0010526 A1 1/2013 Ramaswamy et al.

FOREIGN PATENT DOCUMENTS

TW 201306219 A 2/2013
WO WO-2011020122 A1 2/2011
WO WO-2013006376 A2 1/2013
WO WO-2013006376 A3 1/2013

OTHER PUBLICATIONS

Cleveland L. Metal Oxide Hetero Junction Operation Nonvolatile Memory, FlashMemory Summit, Cleveland 2012.*

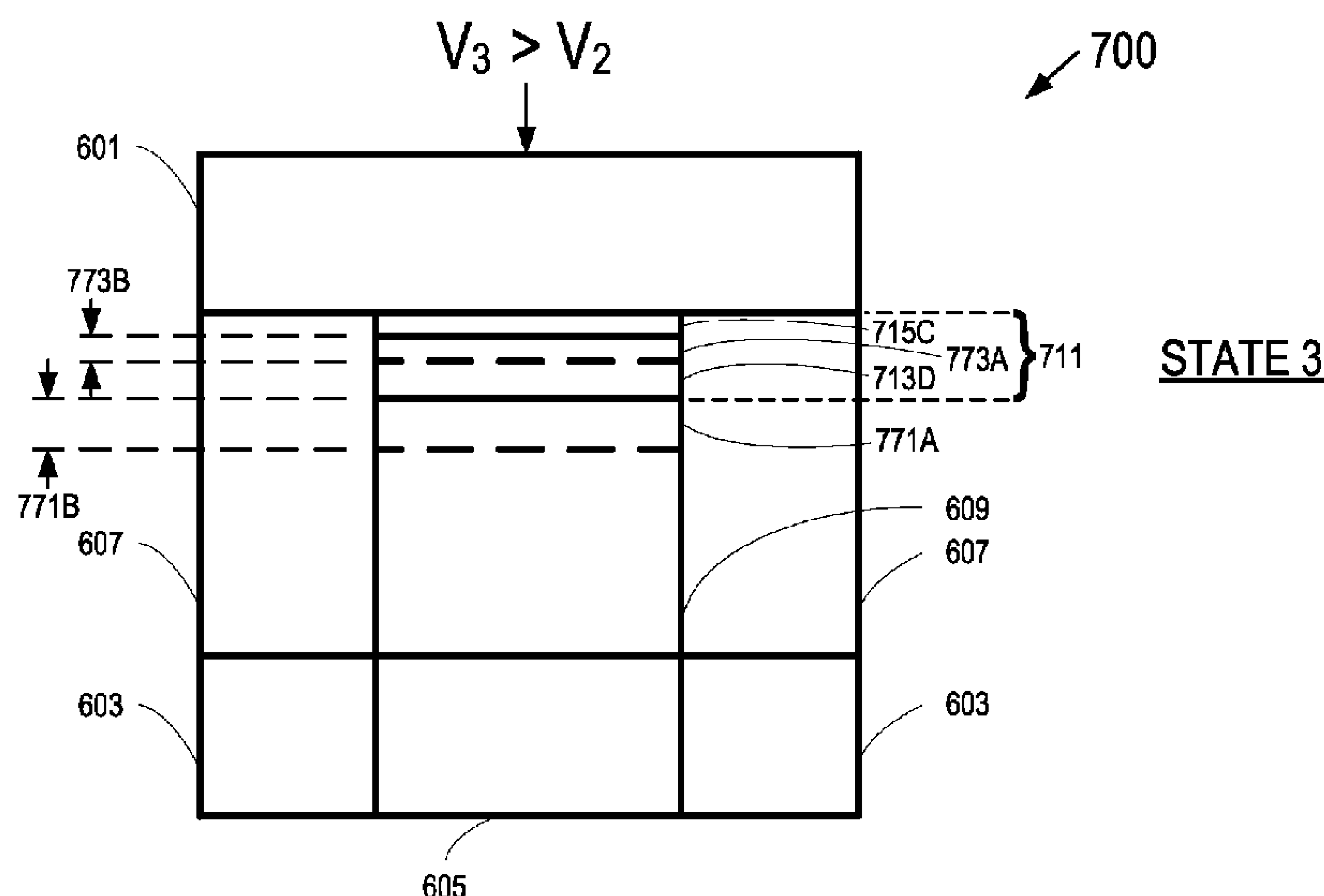
(Continued)

Primary Examiner — Thomas L Dickey
Assistant Examiner — Joseph Schoenholtz
(74) *Attorney, Agent, or Firm* — Schwegman, Lundberg & Woessner, P.A.

(57) **ABSTRACT**

Various embodiments include a memory device and methods of forming the same. The memory device can include an electrode coupled to one or more memory elements, to store information. The electrode may comprise a number of metals, where a first one of the metals has a Gibbs free energy for oxide formation lower than the Gibbs free energy of oxidation of a second one of the metals.

26 Claims, 11 Drawing Sheets



(56) **References Cited**

OTHER PUBLICATIONS

Liao, Z. L., Z. Z. Wang, Y. Meng, Z. Y. Liu, P. Gao, J. L. Gang, H. W. Zhao, X. J. Liang, X. D. Bai, and D. M. Chen. "Categorization of Resistive Switching of Metal-Pr0.7Ca0.3MnO3-metal Devices." Applied Physics Letters 94.25 (2009): 253503.*

Oxidation-Reduction (Redox) Reactions and Potentials downloaded from URL<http://scholar.lib.vt.edu/theses/available/etd-01102003-162857/unrestricted/(08)Lit_Rev_2.pdf> on Dec. 27, 2012.*

Periodical Tabel of Elements Ti, downloaded from URL<http://www.periodni.com/ti.html> on Dec. 27, 2012.*

Periodical Tabel of Elements Pt, downloaded from URL<http://www.periodni.com/ti.html> on Dec. 27, 2012.*

Kim, D. S., C. E. Lee, Y. H. Kim, and Y. T. Kim. "Effect of Oxygen Annealing on Pr[sub 0.7]Ca[sub 0.3]MnO[sub 3] Thin Film for Colossal Electroresistance at Room Temperature." Journal of Applied Physics 100.9 (2006): 093901.*

Ellingham Diagram downloaded from URL <http://web.deu.edu.tr/metalurjimalzeme/pdf/MMM2003MetalurjiTermodinamigi/EllinghamKaynak2.pdf> on Dec. 27, 2012.*

Jian-Lei, Gang, Li Song-Lin, Liao Zhao-Liang, Meng Yang, Liang Xue-Jin, and Chen Dong-Min. "Clockwise vs Counter-Clockwise-Hysteresis of Point-Contact Metal-Tip/PrCaMnO/Pt Devices." Chinese Physics Letters 27.2 (2010).*

Asanuma, S., and H. Akoh. "Relationship between Resistive Switching Characteristics and Band Diagrams of Ti/Pr1—xCaxMnO3 Junctions." Physical Review B 80.23 (2009).*

Tedulkar, Mihir, Impact of Hydrogen on the Forming and Switching Behaviors of PCMO Thin Films for Resistance Change Random Access Memory. Diss. Stanford, 2011. Stanford: Stanford University, May 2011.*

Burr, Geoffrey, et. al.. "Phase Change Memory Technology." Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures 28.2 (2010) 223.*

Kaji H,, et. al. Effect of electrode and interface oxide on the property of ReRAM composed of Pr0.7Ca0.3MnO3 IOP Conf. Series: Materials Science and Engineering 8 (2010) 012032.*

Kawano, Hiroyasu, Keiji Shono, Takeshi Yokota, and Manabu Gomi. "Enhancement of Switching Capability on Bipolar Resistance Switching Device with Ta/PrCaMnO/Pt Structure." Applied Physics Express 1 (2008): 101901.*

Shono, Keiji, Hiroyasu Kawano, Takeshi Yokota, and Manabu Gomi. "Origin of Negative Differential Resistance Observed on Bipolar Resistance Switching Device with Ti/PrCaMnO/Pt Structure." Applied Physics Express 1 (2008): 055002.*

H.-S. P. Wong, et. al., "Phase Change Memory" Proc. IEEE 98, 2201 (2010).*

R. Yasuhara, T. Yamamoto, I. Ohkubo, H. Kumigashira, and M. Oshima, Appl. Phys. Lett. 97, 132111 (2010).*

Hwang, Hyunsang "Electrical and Reliability Characteristics of RRAM for Cross-point Memory Applications" 7th International Symposium on Advanced Gate Stack Technology Sematech Sep. 29, 2010 Albany NY.*

W. Lee, G. Jo, S. Lee, J. Park, M. Jo, J. Lee, S. Jung, S. Kim, J. Shin, S. Park, T. Lee, and H. Hwang, Appl. Phys. Lett. 98, 032105 (2011).*

International Application Serial No. PCT/US2012/044653, International Search Report mailed Jan. 25, 2013, 3 pgs.

International Application Serial No. PCT/US2012/044653, Written Opinion mailed Jan. 25, 2013, 6 pgs.

* cited by examiner

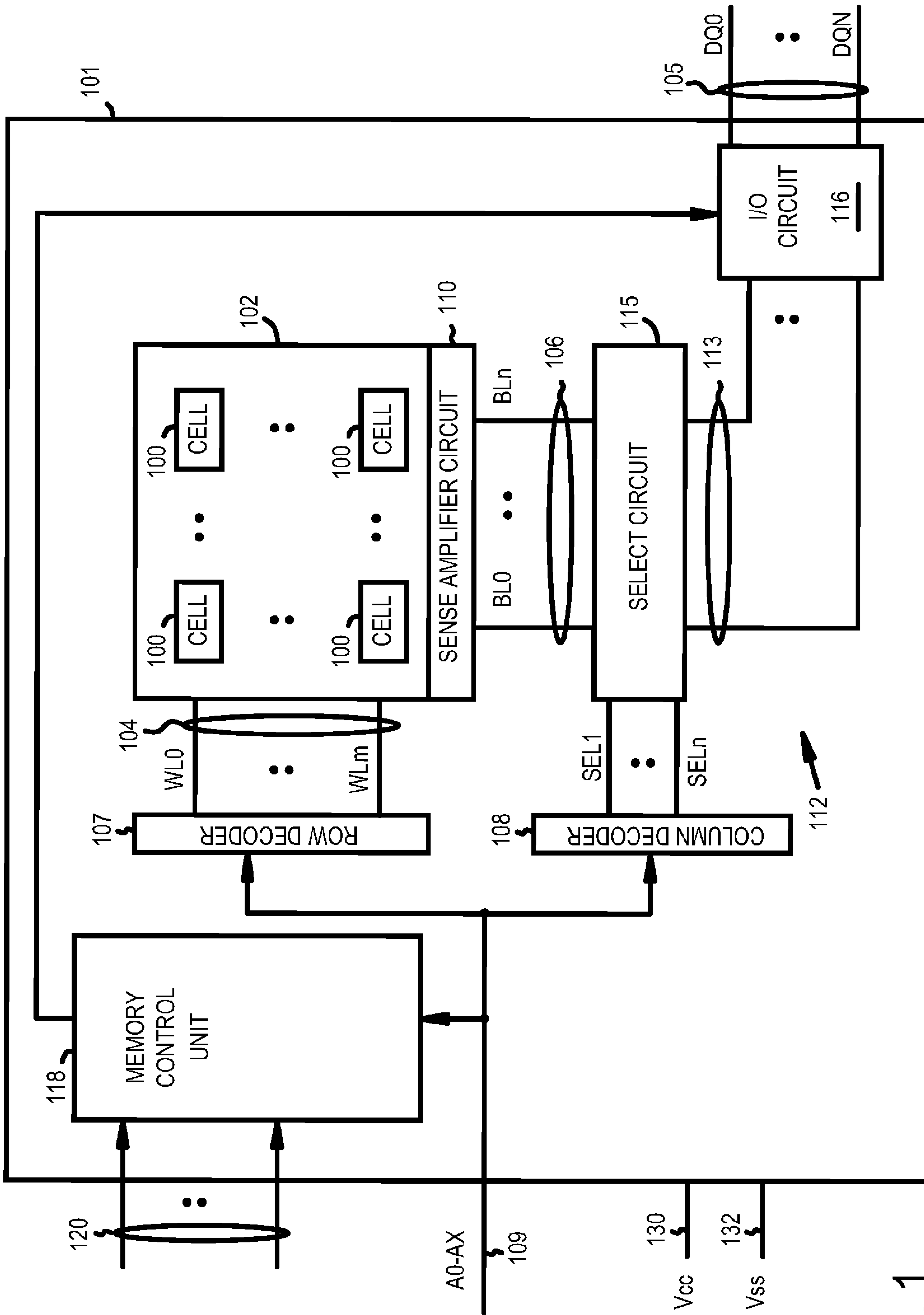


FIG. 1

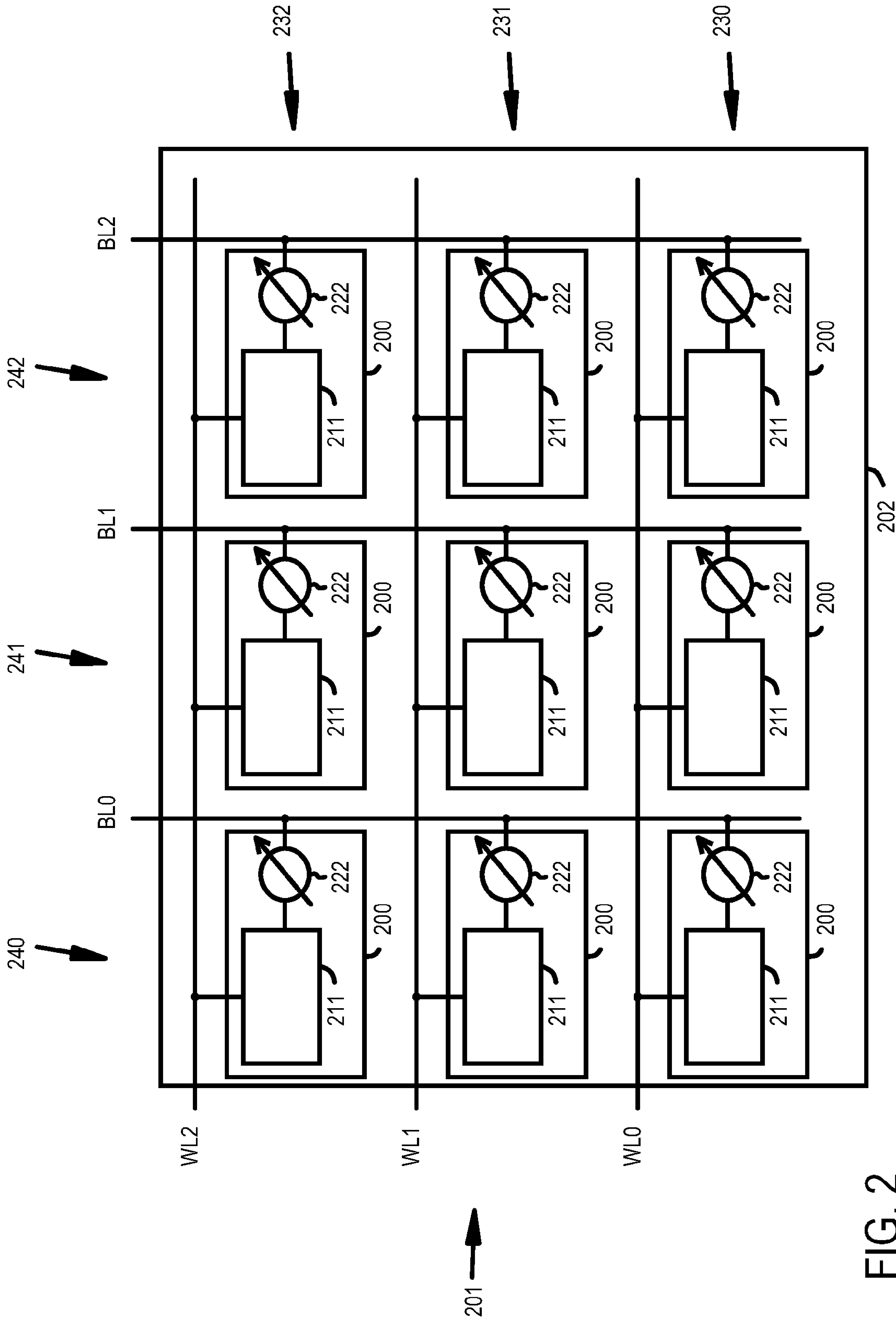


FIG. 2

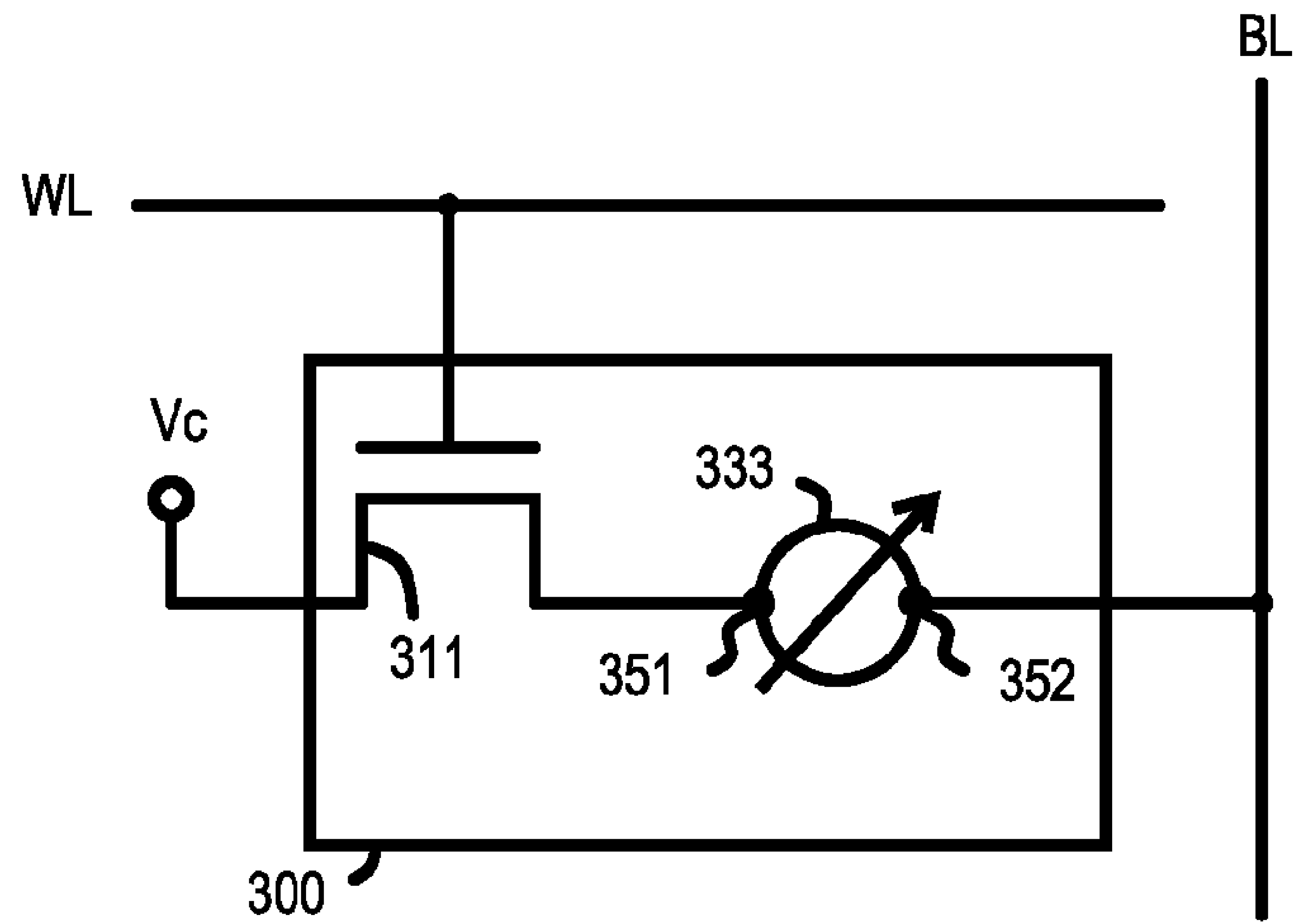


FIG. 3

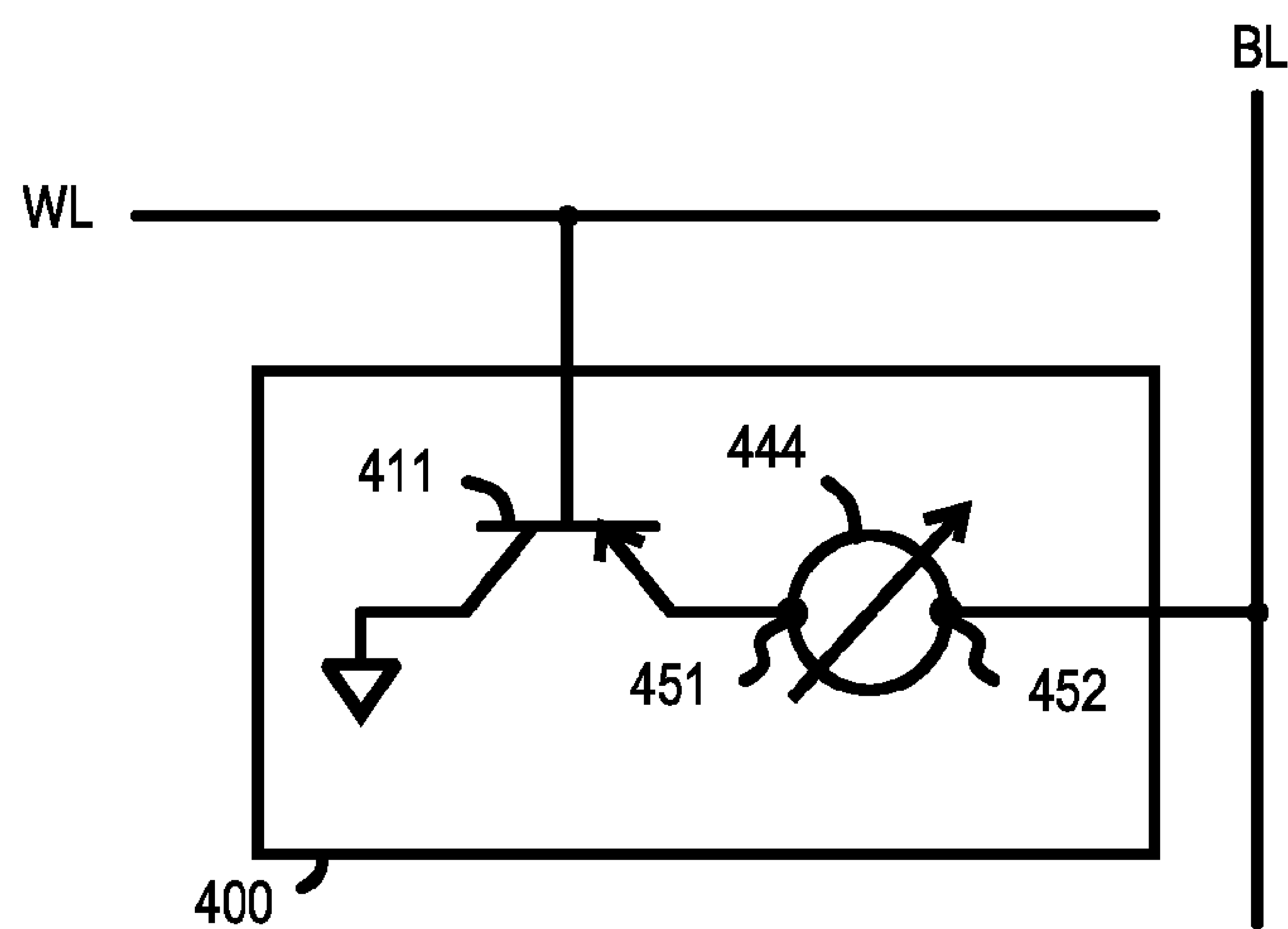


FIG. 4

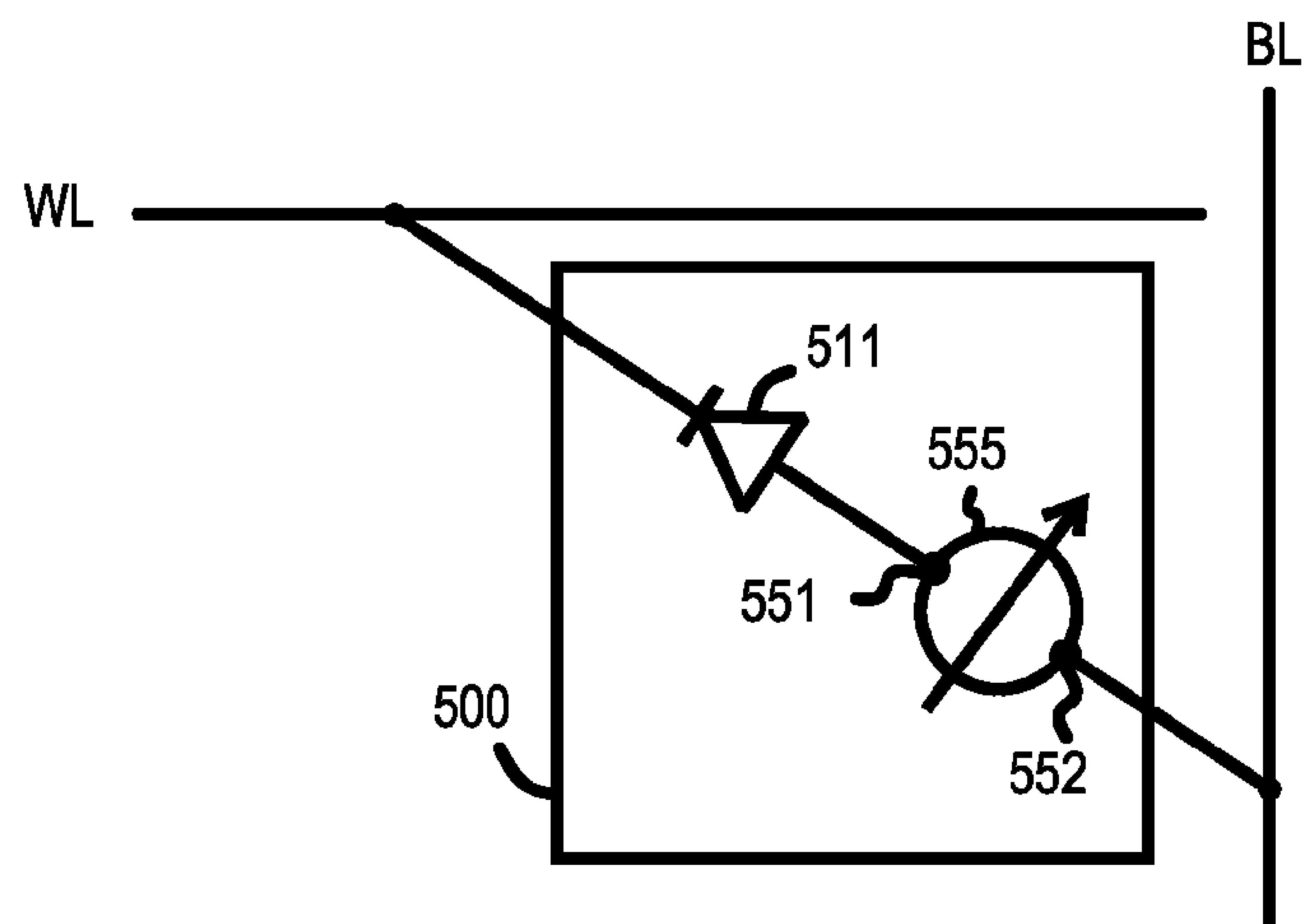


FIG. 5

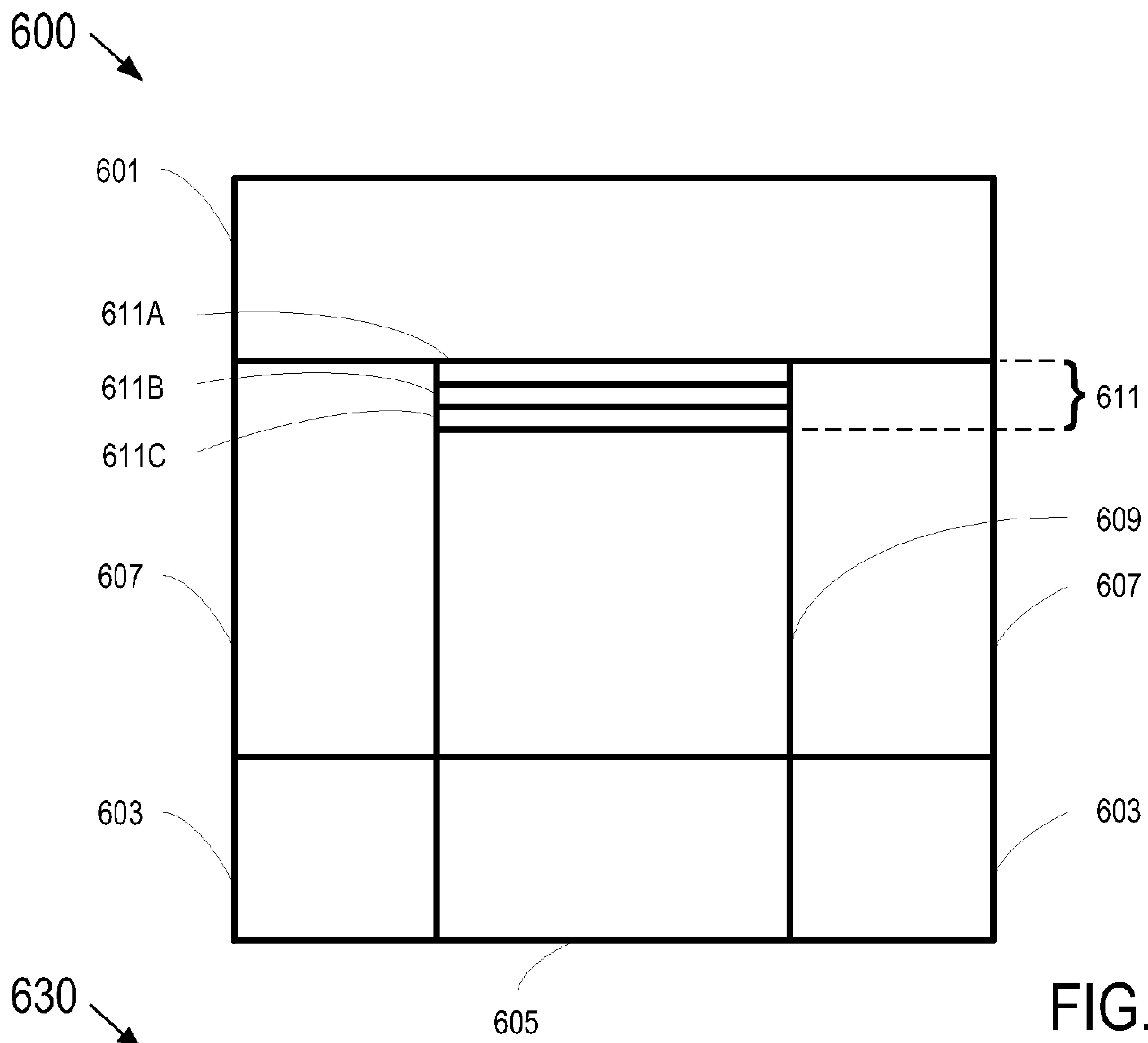


FIG. 6A

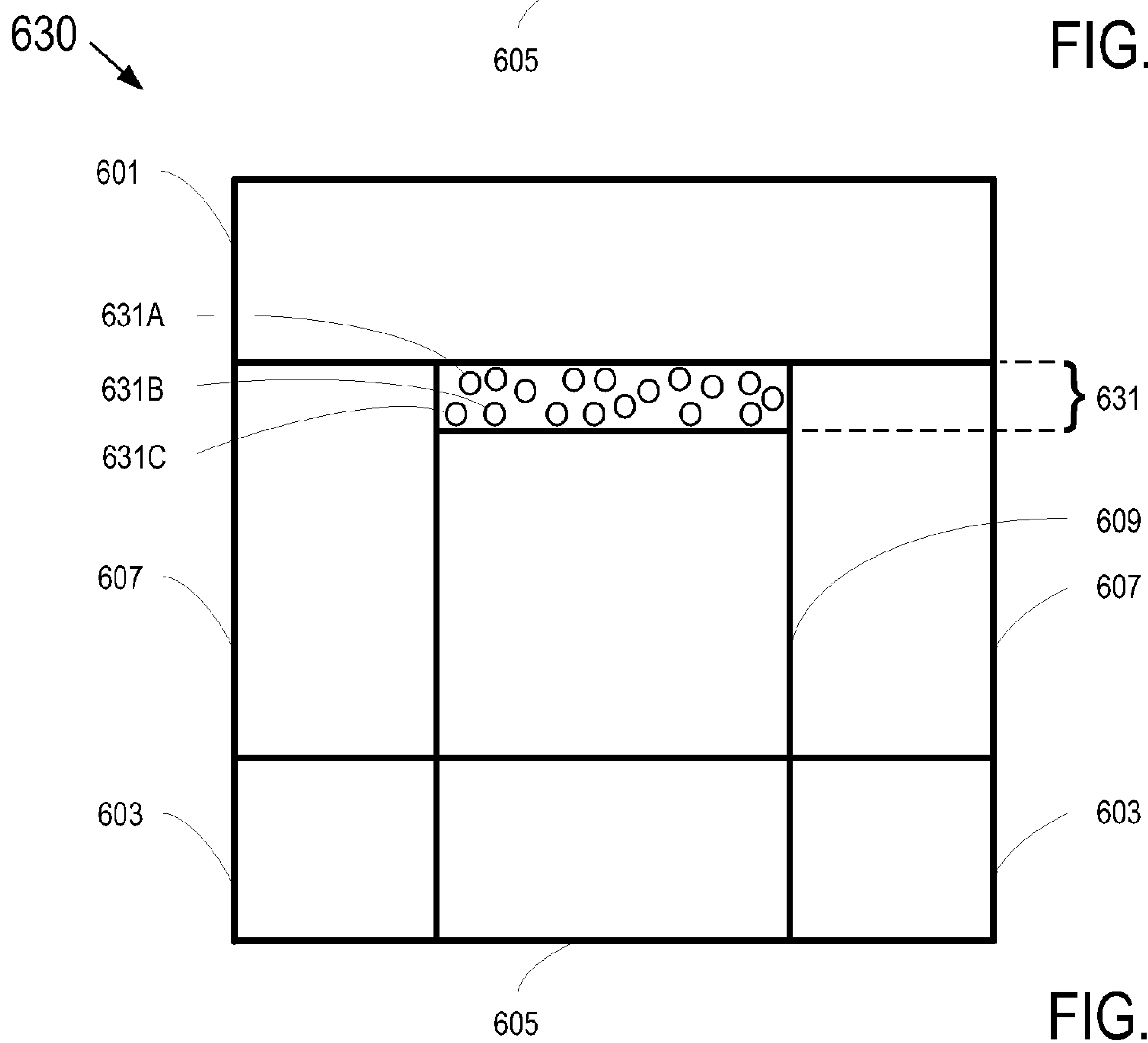


FIG. 6B

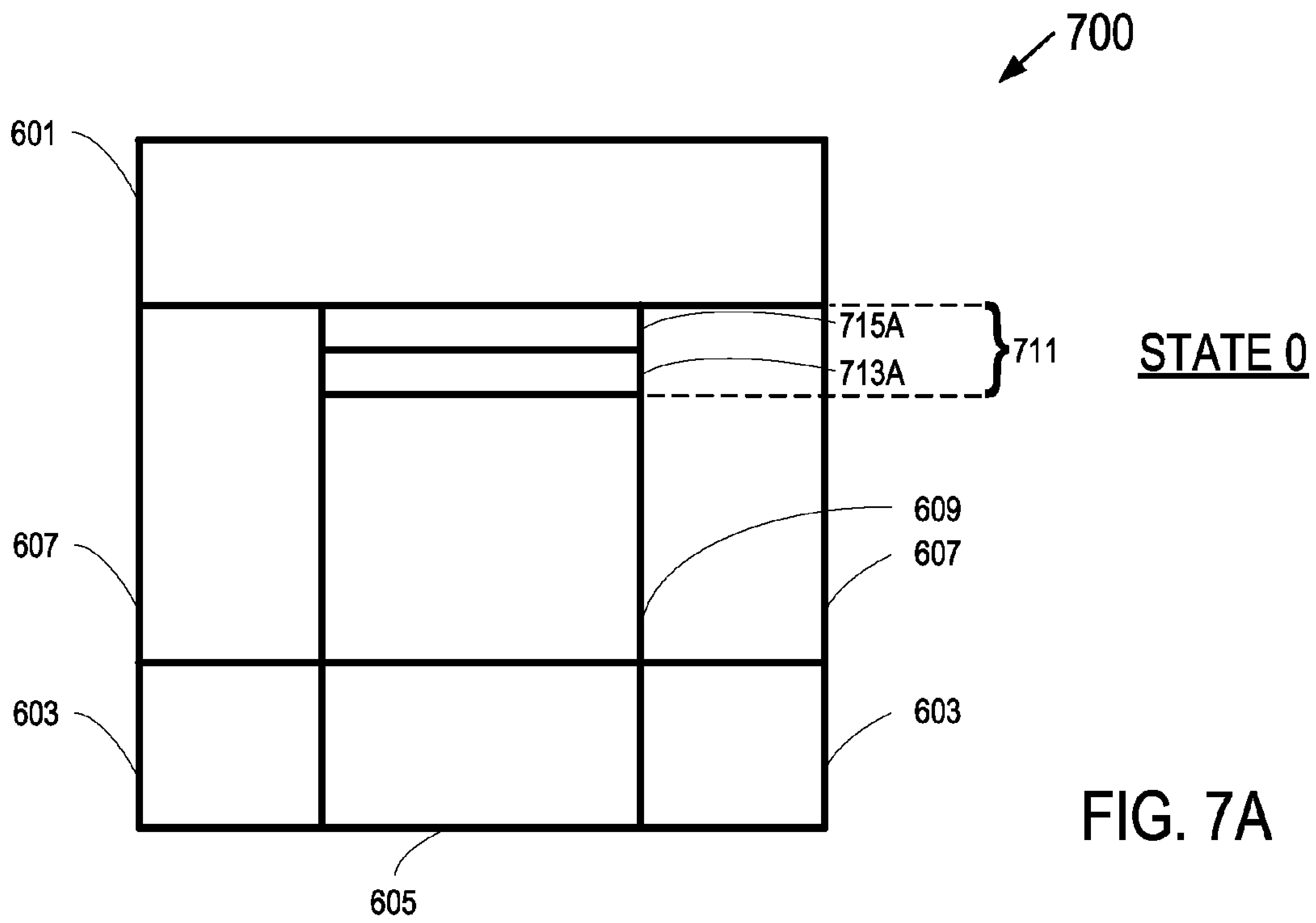


FIG. 7A

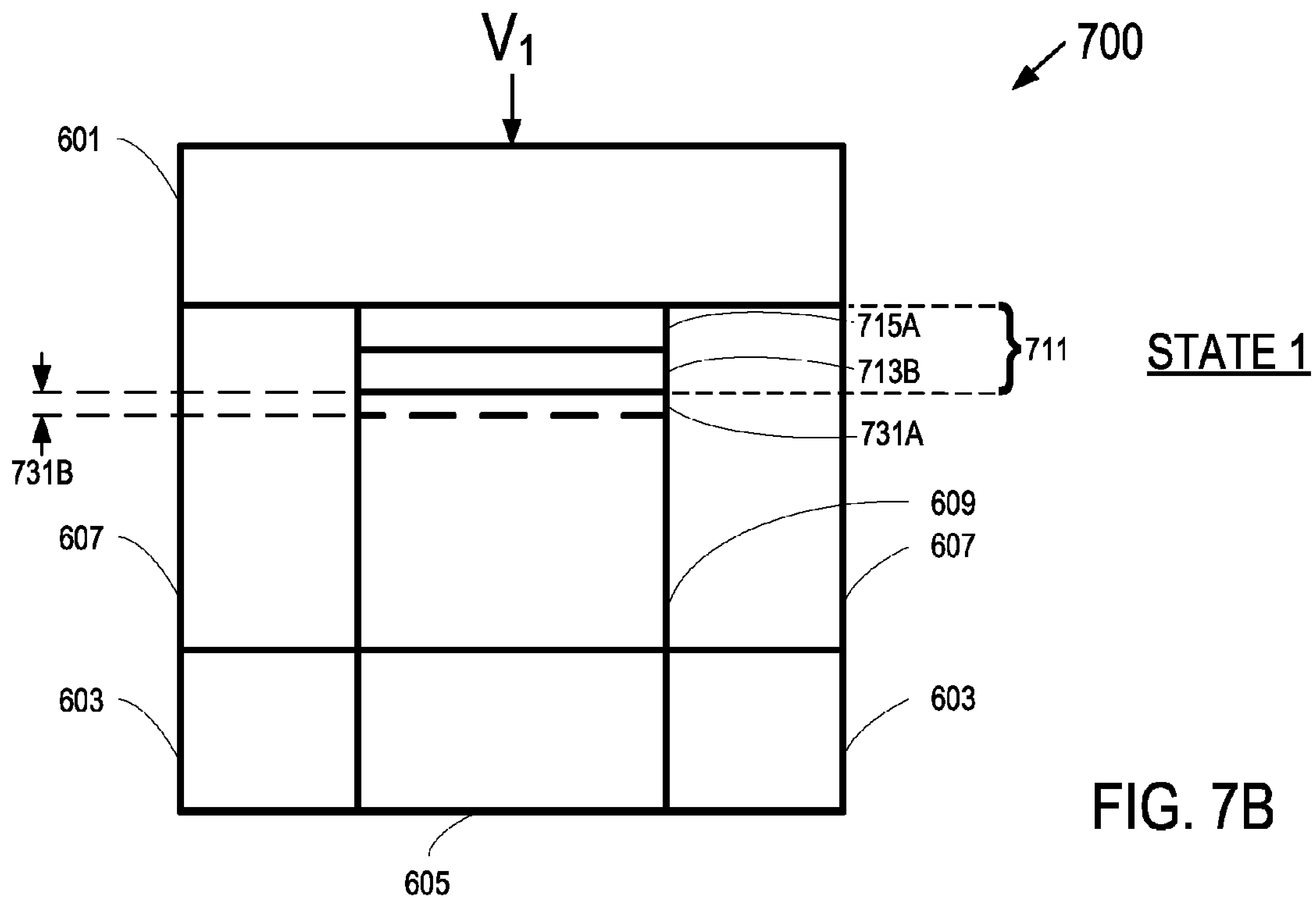


FIG. 7B

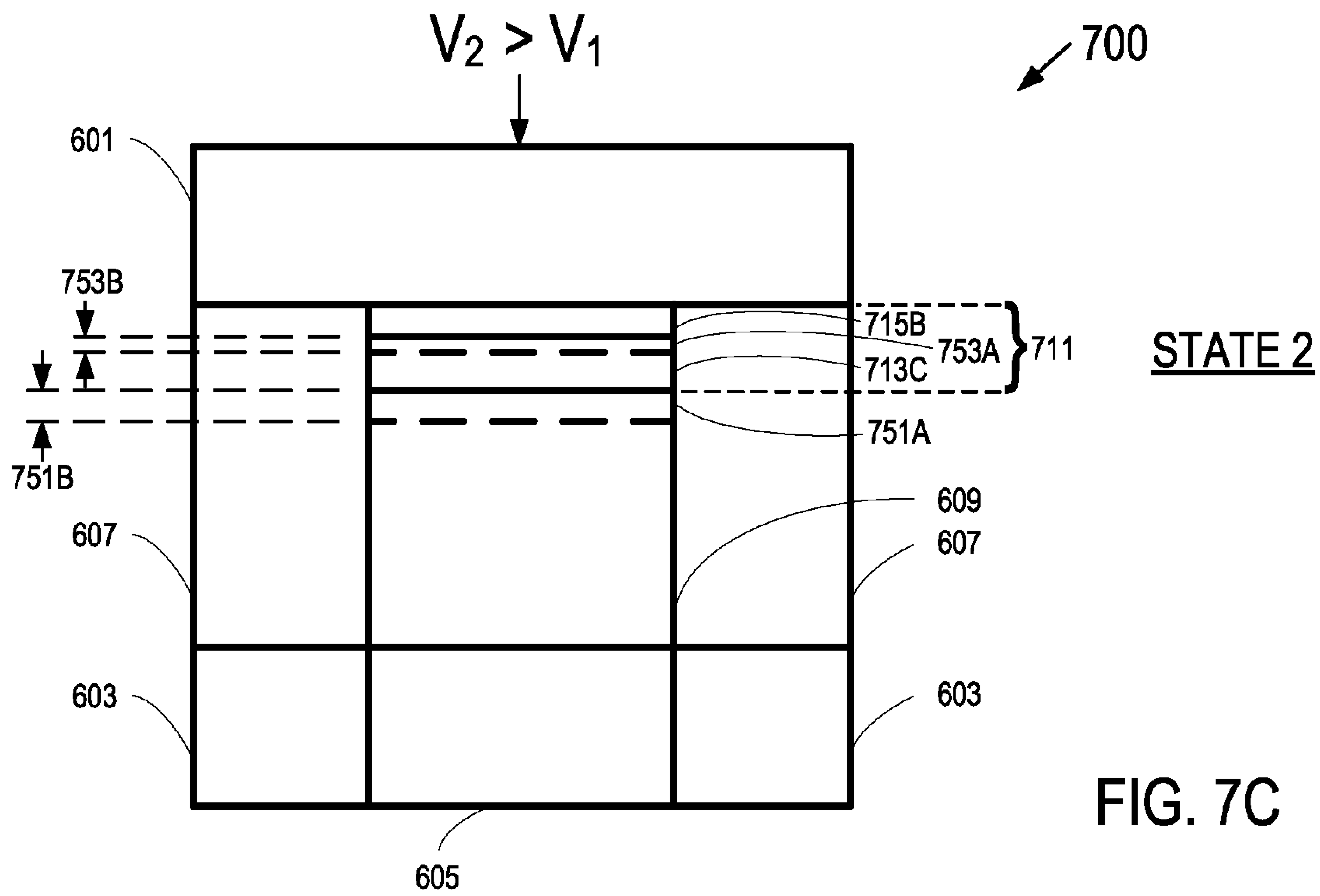


FIG. 7C

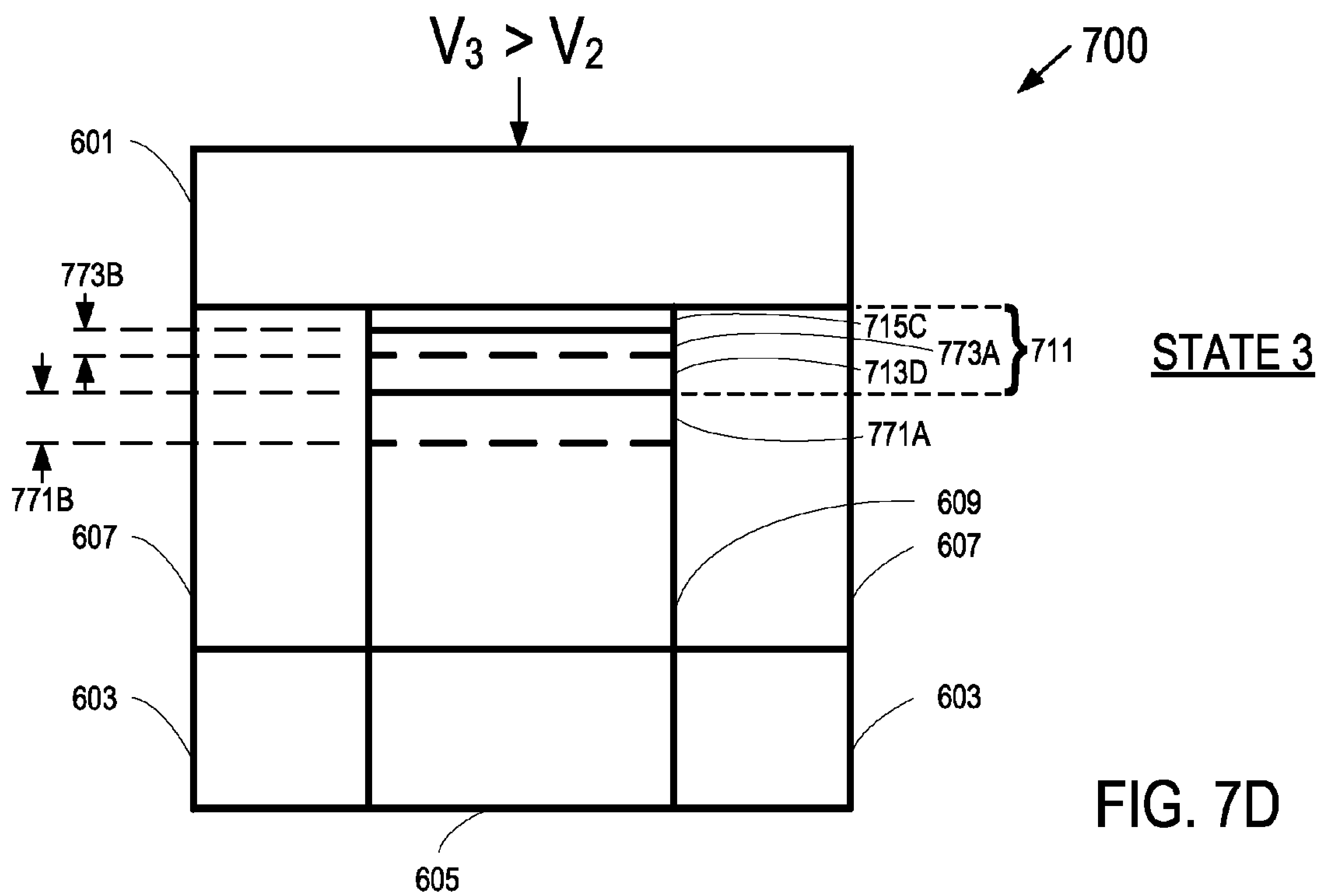


FIG. 7D

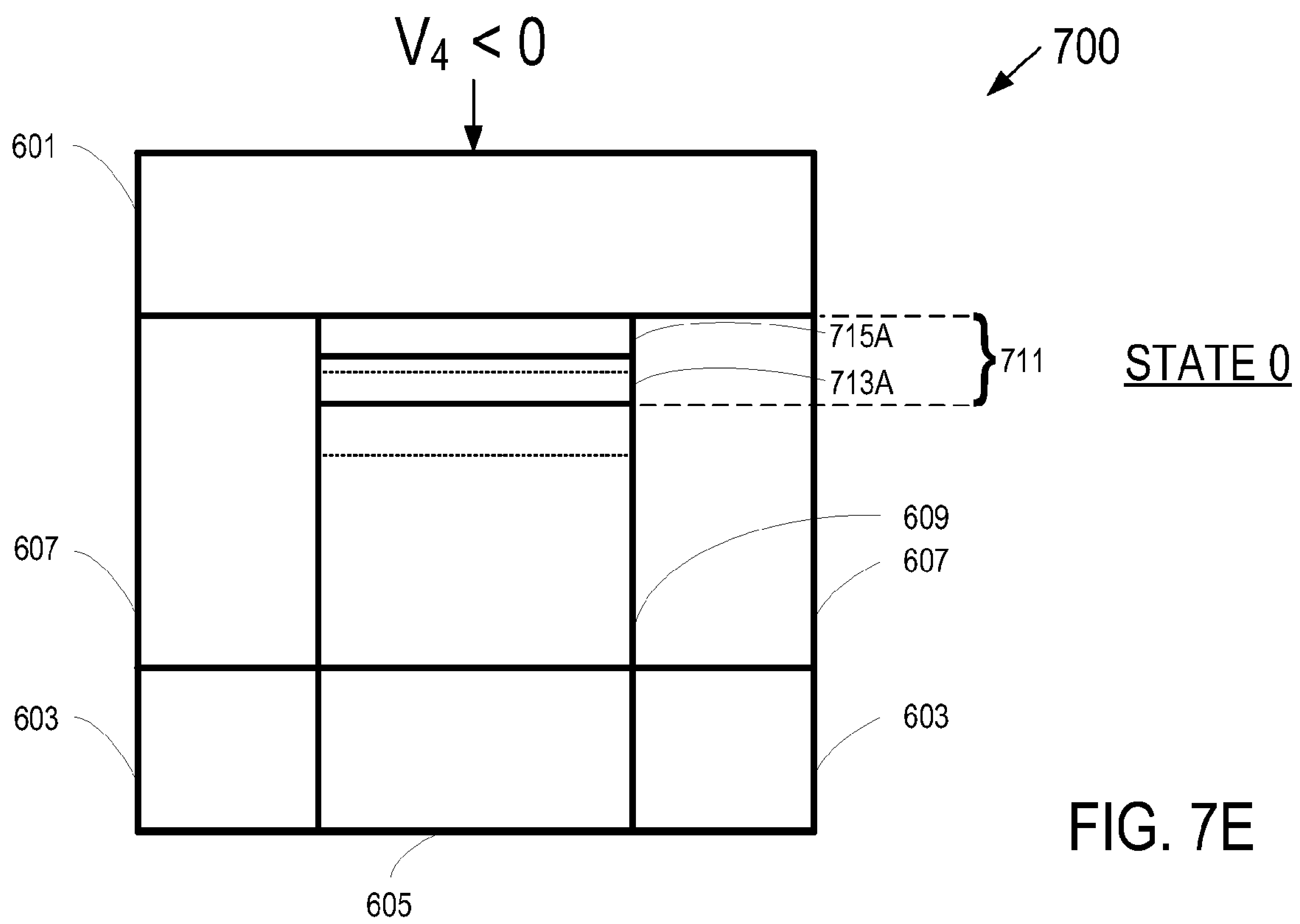


FIG. 7E

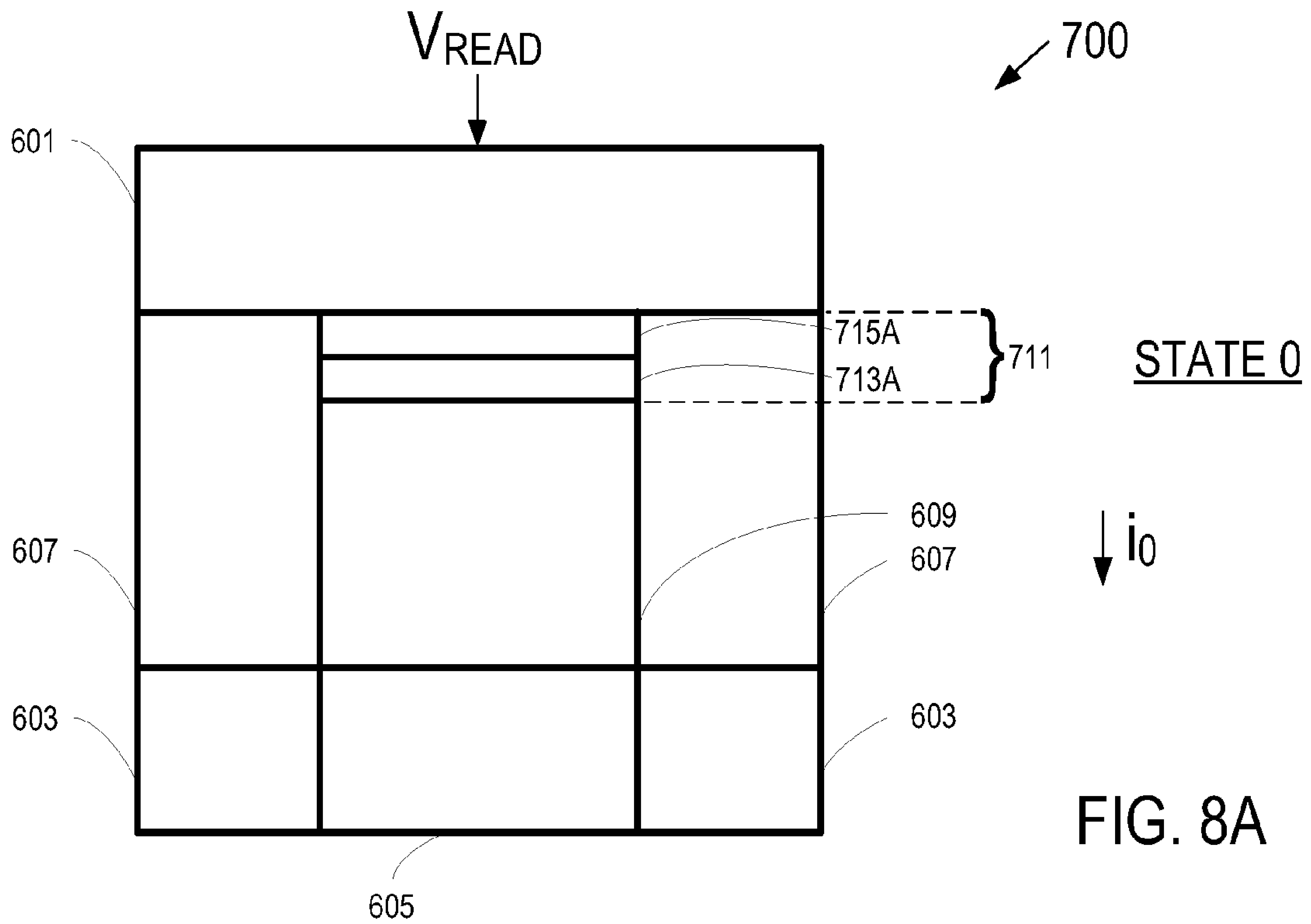


FIG. 8A

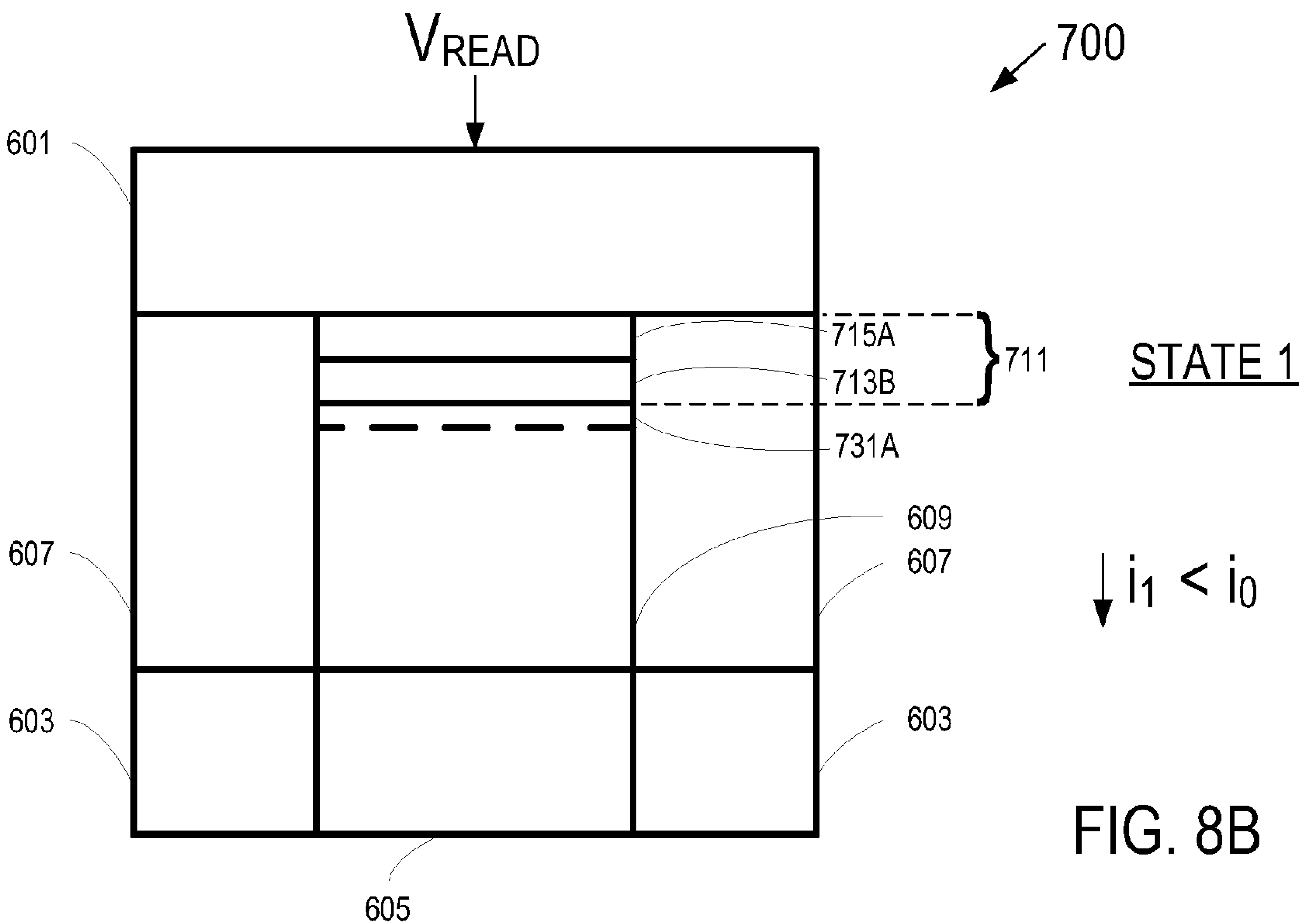


FIG. 8B

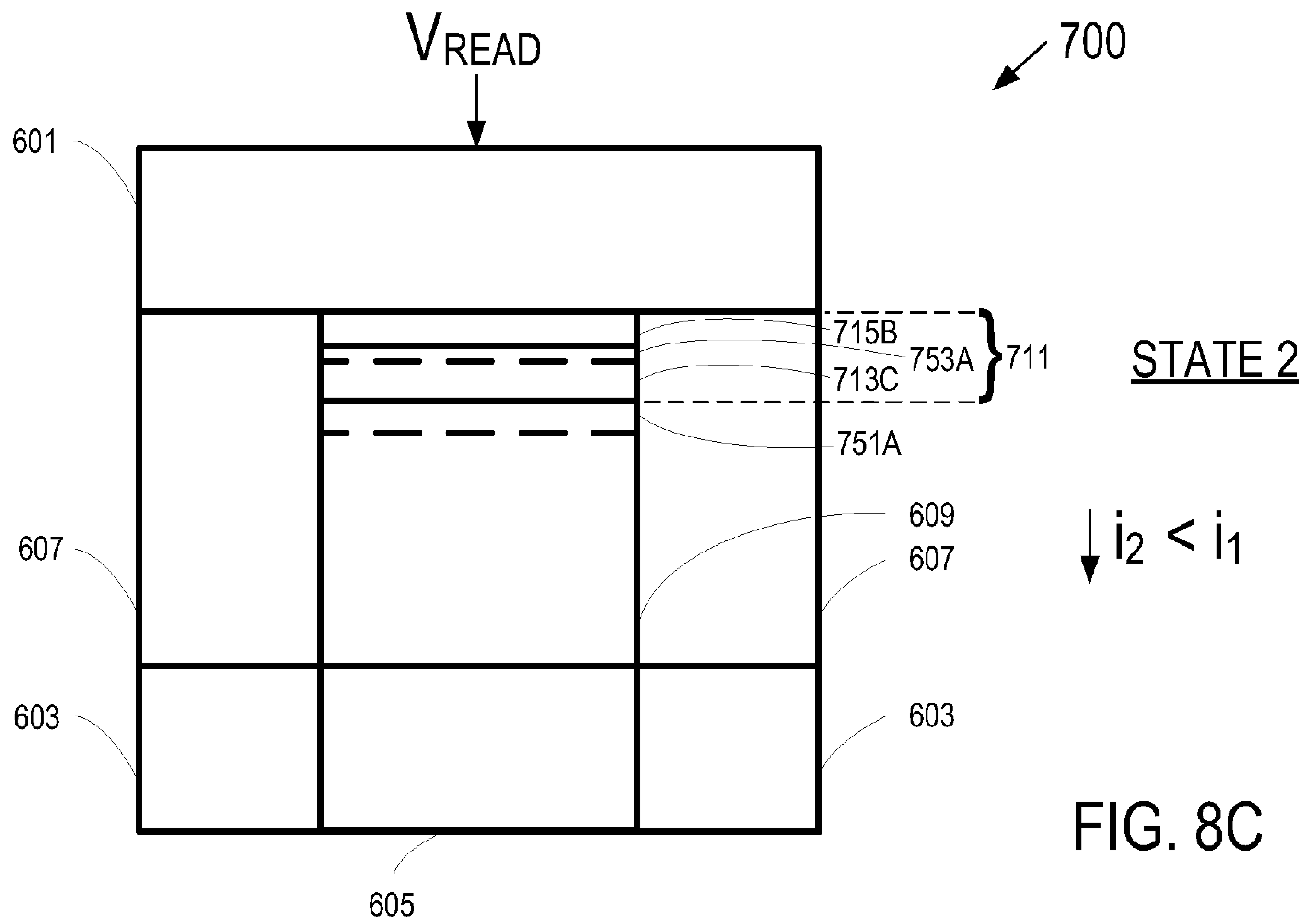


FIG. 8C

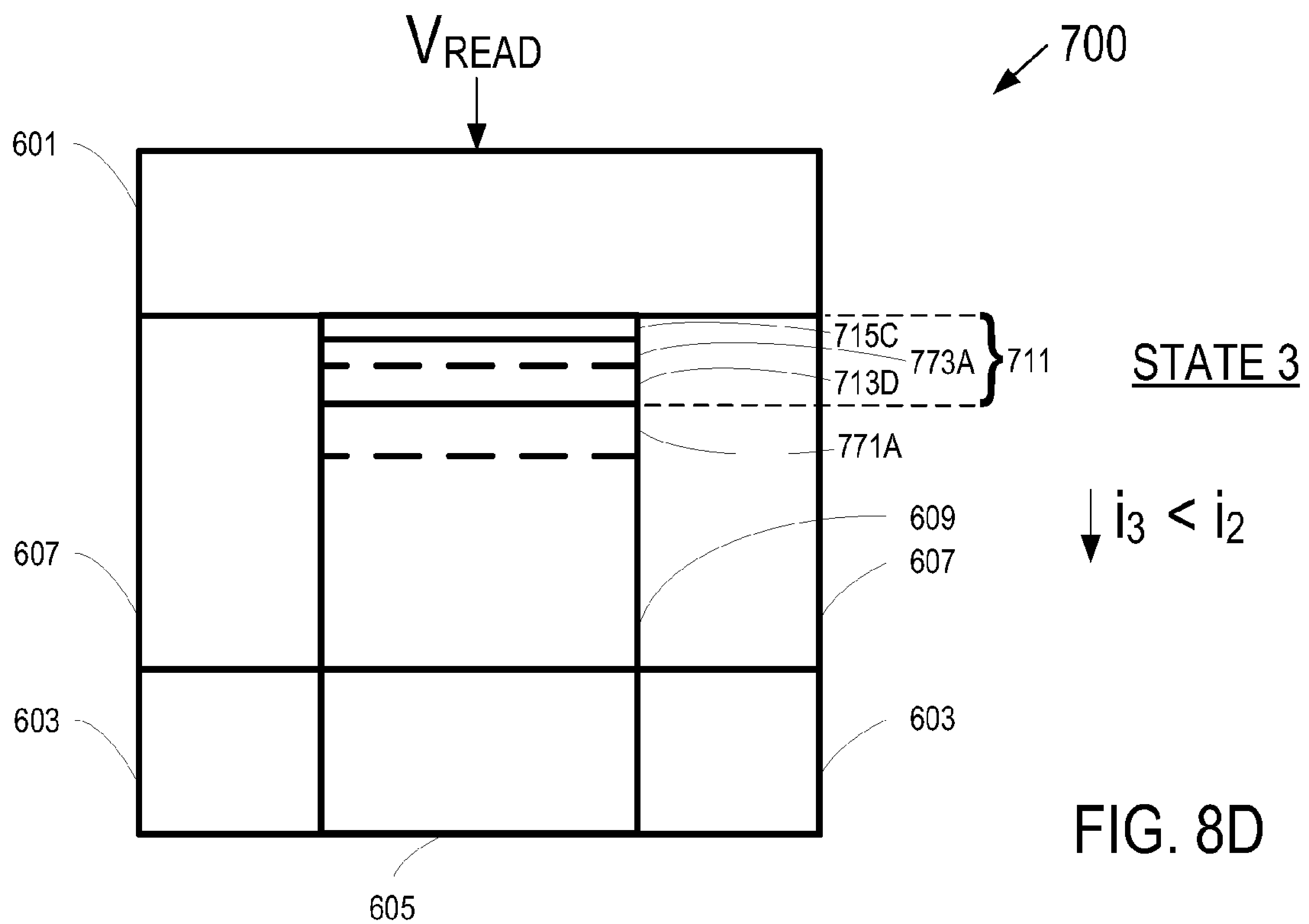


FIG. 8D

FIG. 9A

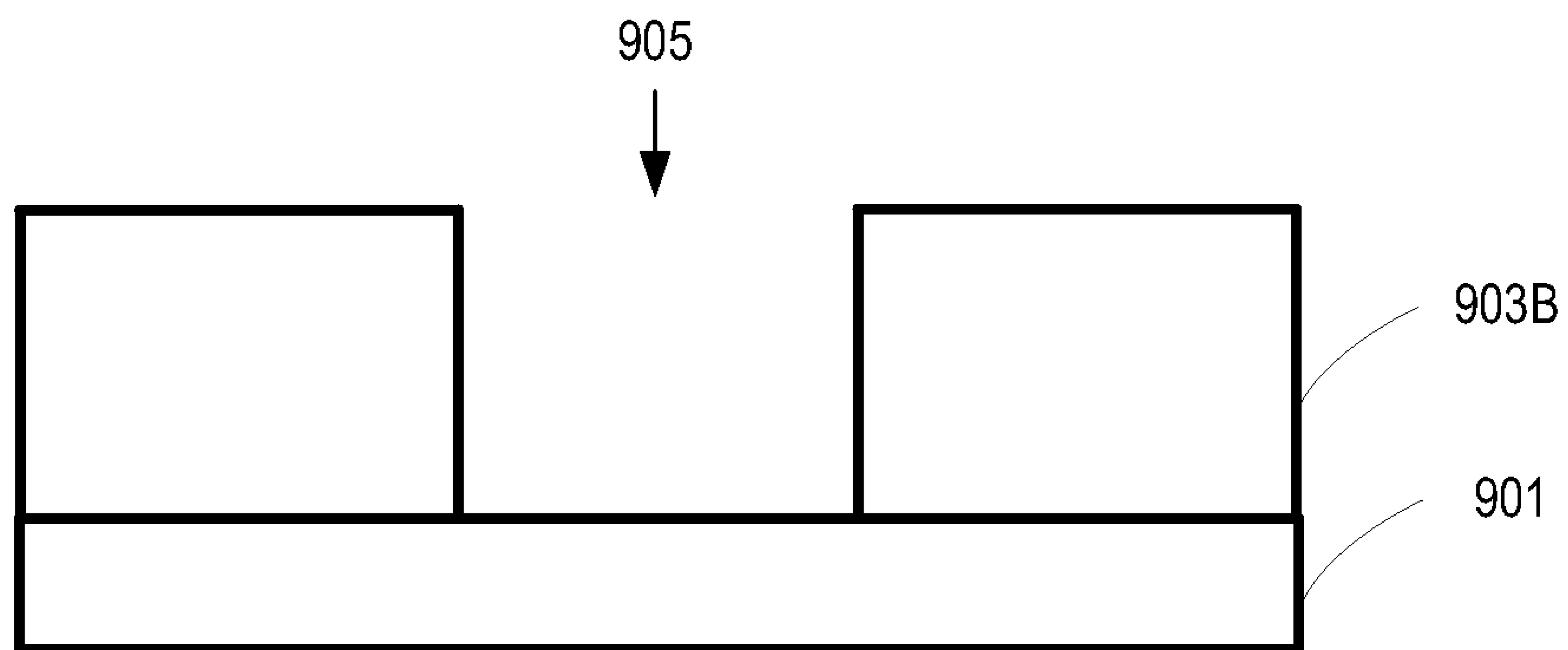


FIG. 9B

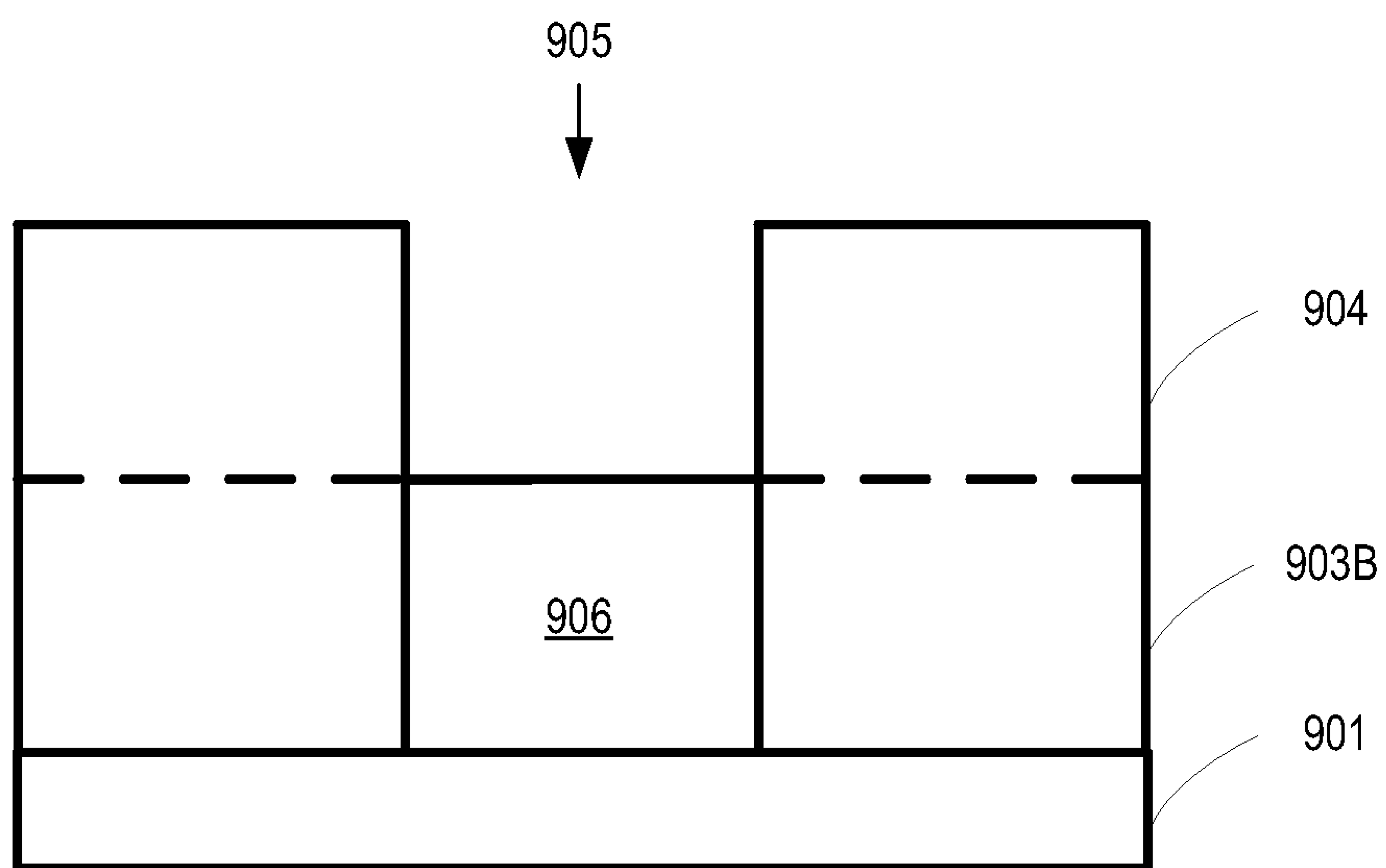


FIG. 9C

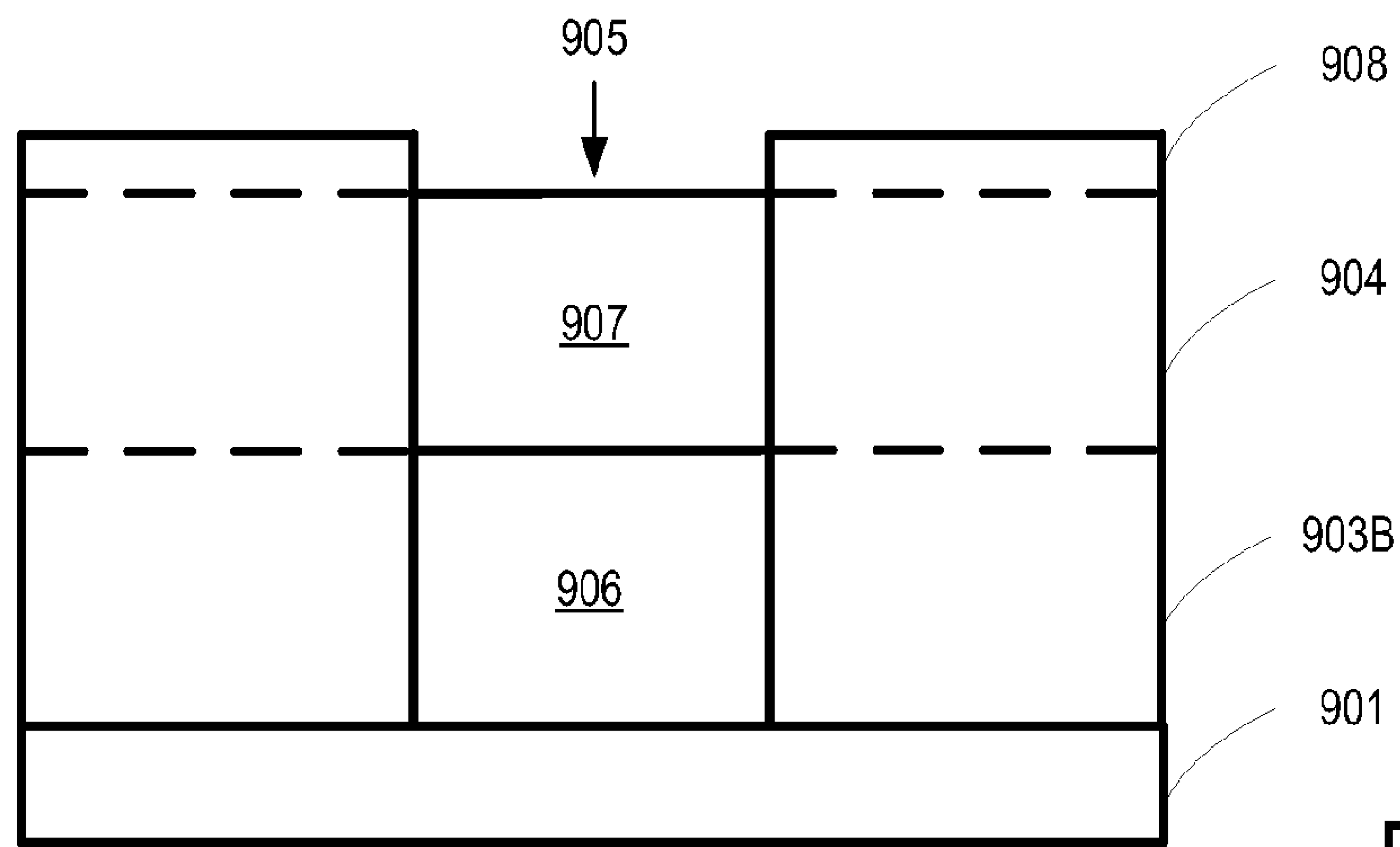


FIG. 9D

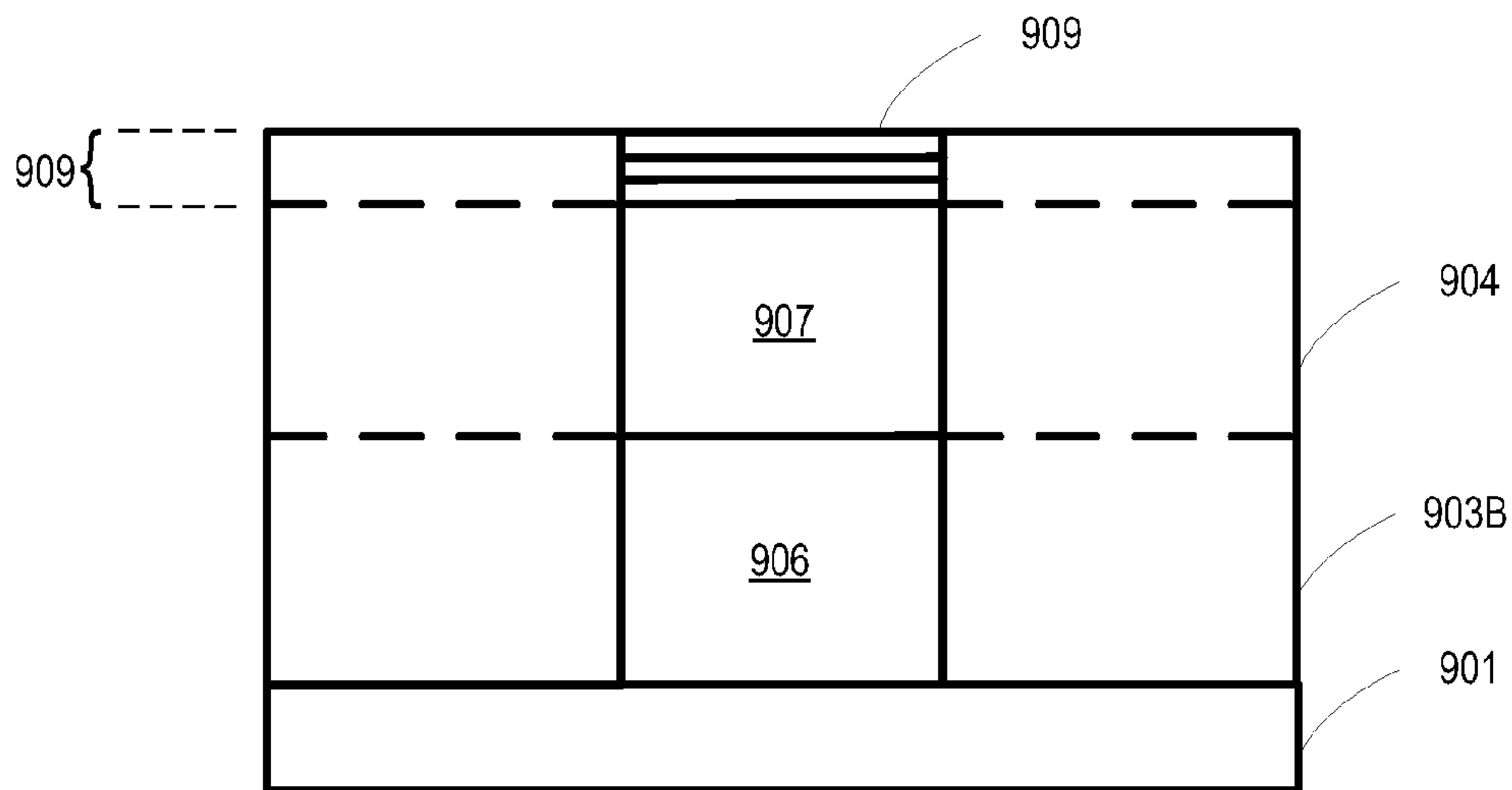


FIG. 9E

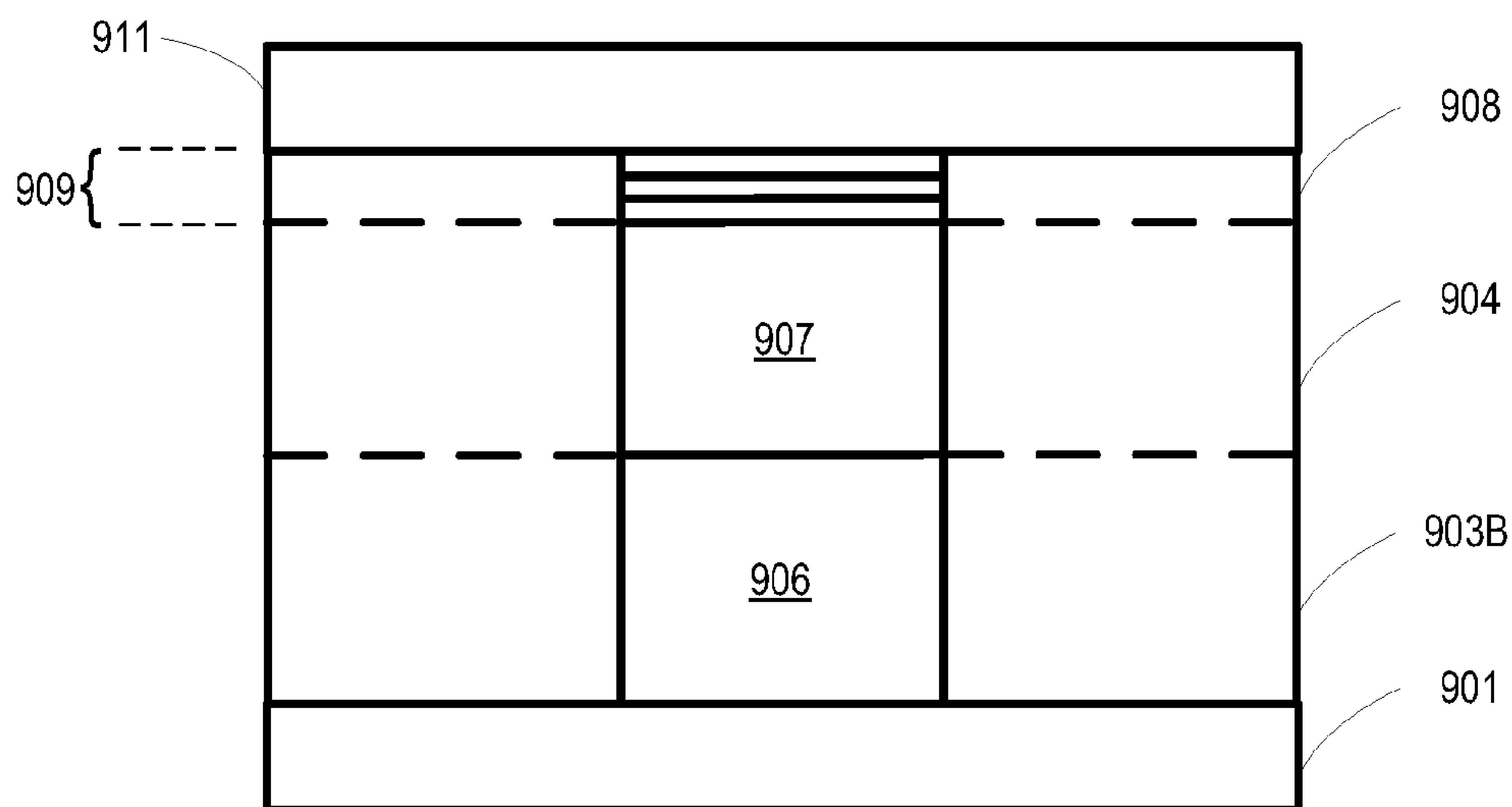


FIG. 9F

MULTILEVEL MIXED VALENCE OXIDE (MVO) MEMORY

BACKGROUND

Computers and other electronic products, for example, digital televisions, digital cameras, and cellular phones, often have one or more memory devices to store information. Some memory devices may have memory cells that are capable of storing multiple bits of information in each memory cell. In some cases, however, producing these types of memory devices may pose challenges.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** shows a block diagram of a memory device having a memory array with memory cells, according to an embodiment;

FIG. **2** shows a partial block diagram of a memory device having a memory array including memory cells with access components and memory elements, according to an embodiment;

FIGS. **3** through **5** show schematic diagrams of examples of different memory cells having different access components coupled to memory elements, according to various embodiments;

FIG. **6**A shows a cross-sectional view of a portion of a memory cell, according to an example embodiment;

FIG. **6**B shows an alternative cross-sectional view of a portion of a memory cell, according to an example embodiment;

FIGS. **7**A through **7**E show a memory cell having various states and resistivity values, according to an example embodiment;

FIGS. **8**A through **8**D show the memory cell of FIGS. **7**A through **7**D having different values of currents flowing from a top electrode to a lower electrode in various read operations, according to an example embodiment; and

FIGS. **9**A through **9**F show various portions of a fabrication process to form a memory cell, according to an example embodiment.

DETAILED DESCRIPTION

The description that follows includes illustrative systems, methods, techniques, and programming sequences that embody the inventive subject matter. In the following description, for purposes of explanation, numerous specific details are set forth in order to provide an understanding of various embodiments of the inventive subject matter. It will be evident, however, to those skilled in the art that various embodiments of the inventive subject matter may be practiced without these specific details. Further, well-known instruction instances, protocols, structures, methods, fabrication technologies, and techniques have not been shown in detail.

As used herein, the term "or" may be construed in an inclusive or exclusive sense. Additionally, although various exemplary embodiments discussed below focus on a multilevel mixed valence oxide (MVO) memory, the embodiments are merely given for clarity in disclosure, and thus, are not limited to multilevel MVO memory. As an introduction to the subject, a few embodiments will be described briefly and generally in the following paragraphs, and then a more detailed description, with reference to the figures, will ensue.

In various embodiments, a memory device is provided that includes at least one memory element to store information, with an electrode coupled to the at least one memory element. The electrode can include a number of metals, where a first one of the metals has a Gibbs free energy for the formation of oxide lower than the Gibbs free energy of oxidation of a second one of the metals.

In embodiments of the memory device, each of the plurality of metals is layered and substantially parallel to a surface of the at least one memory element coupled to the plurality of metals. In embodiments, the plurality of metals is dispersed substantially randomly over a surface of the at least one memory element coupled to the plurality of metals. In embodiments, the at least one memory element is configured to store multiple bits of information. In embodiments, the memory device further includes a second electrode coupled to the at least one memory element such that the at least one memory element is disposed between the second electrode and the first electrode. In embodiments, the at least one memory element includes at least one of $Pr_xCa_yMn_zO$, $La_xCa_yMnO_z$, $La_xSr_yCo_xY$, TiO_x, HfO_x, or ZrO_x. In embodiments, the at least one memory element includes a mixed valence oxide.

In various embodiments, a memory device is provided that includes a number of metals. The number of metals includes a first metal having a Gibbs free energy of oxidation lower than the Gibbs free energy of oxidation of a second metal. A memory element in the device is electrically coupled to the metals such that the memory element provides oxygen atoms to the metals when a bias voltage is applied across the memory element and the metals. The memory element is at least partially comprised of a mixed valence oxide.

In embodiments of the memory device, the Gibbs free energy of the first metal of the plurality of metals is more negative than a Gibbs free energy of the memory element. In embodiments, the memory device further includes a first electrode and a second electrode, with the plurality of metals and the memory element being disposed between the first electrode and the second electrode. In embodiments, the memory element is configured to store bits of information. In embodiments, the memory element includes oxygen.

In various embodiments, a memory device is provided that includes a first electrode for coupling to a first voltage supply terminal, at least one memory element coupled to the first electrode comprising a mixed valence oxide, and a second electrode for coupling to a second voltage supply terminal. The second electrode includes a number of metals electrically coupled to the at least one memory element. The metals include at least one metal oxide to store information in the at least one memory element in response to an electrical bias generated by a voltage supply coupled to the first and second electrodes.

In embodiments of the memory device, a first metal of the plurality of metals has a Gibbs free energy of oxidation lower than a Gibbs free energy of oxidation of a second metal of the plurality of metals. In embodiments, the at least one memory element includes a material having oxygen.

In various embodiments, a method of forming a memory device is described, including forming a memory material on a substrate and forming a first metal over the memory material. The first metal has a Gibbs free energy of oxidation more negative than a Gibbs free energy of the memory material. A second metal is formed over the memory material with the second metal having a Gibbs free energy more negative than the Gibbs free energy of the first metal. The memory device is annealed to at least partially oxidize the first metal but not necessarily the second metal.

In embodiments of the method of forming a memory device, the method includes supplying oxygen atoms to oxidize the first metal and the second metal from the memory

material. In embodiments, the method includes supplying gaseous oxygen to the memory device during the annealing to supply oxygen atoms to oxidize the first metal and the second metal. In embodiments, the method includes forming the first metal and the second metal in alternate layers. In embodiments, the method includes forming the first metal and the second metal concurrently.

In various embodiments, a method of forming a memory device is described, including forming a mixed valence oxide on a substrate, forming a first metal over the mixed valence oxide, forming a second metal over the mixed valence oxide, and at least partially oxidizing the first metal with oxygen atoms from the mixed valence oxide.

In embodiments of the method of forming a memory device, the forming of the first metal and the second metal over the mixed valence oxide includes forming the first metal having a Gibbs free energy of oxidation more negative than a Gibbs free energy of the mixed valence oxide, and forming the second metal having a Gibbs free energy of oxidation more negative than the Gibbs free energy of oxidation of the first metal. In embodiments, the method includes forming the first metal and the second metal consecutively. In embodiments, the method includes forming the first metal and the second metal concurrently. In embodiments, the first metal and the second metal include different metal materials.

Referring now to FIG. **1**, a block diagram of a memory device **101** is shown. The memory device **101** is shown to include a memory array **102** having a plurality of memory cells **100** according to an embodiment. The memory cells **100** can be arranged in rows and columns along with access lines **104** (e.g., wordlines to conduct signals WL**0** through WLm) and first data lines **106** (e.g., bit lines to conduct signals BL**0** through BLn). The memory device **101** can use the access lines **104** and the first data lines **106** to transfer information to and from the memory cells **100**. A row decoder **107** and a column decoder **108** decode address signals A**0** through AX on address lines **109** to determine which ones of the memory cells **100** are to be accessed.

A sense amplifier circuit **110** operates to determine a value of information read from the memory cells **100** and the information in the form of signals to the first data lines **106**. The sense amplifier circuit **110** can also use the signals on the first data lines **106** to determine values of information to be written to the memory cells **100**.

The memory device **101** is further shown to include circuitry **112** to transfer information between the memory array **102** and input/output (I/O) lines **105**. Signals DQ**0** through DQN on the I/O lines **105** can represent information read from or written into the memory cells **100**. The I/O lines **105** can include nodes within the memory device **101** (or alternatively, pins, solder balls, or other interconnect technologies such as controlled collapse chip connection (C**4**), or flip chip attach (FCA)) on a package where the memory device **101** can reside. Other devices external to the memory device **101** (e.g., a memory controller or a processor, not shown in FIG. **1**) can communicate with the memory device **101** through the I/O lines **105**, the address lines **109**, or control lines **120**.

The memory device **101** can perform memory operations, such as a read operation, to read information from selected ones of the memory cells **100** and a programming operation (also referred to as a write operation) to program (e.g., to write) information into selected ones of the memory cells **100**. The memory device **101** can also perform a memory erase operation to clear information from some or all of the memory cells **100**. A memory control unit **118** controls memory operations based on signals on the control lines **120**. Examples of the signals on the control lines **120** can include one or more clock signals and other signals to indicate which operation (e.g., a programming or read operation) the memory device **101** can or should perform. Other devices external to the memory device **101** (e.g., a processor or a memory controller) can control the values of the control signals on the control lines **120**. Specific values of a combination of the signals on the control lines **120** can produce a command (e.g., a programming or read command) that can cause the memory device **101** to perform a corresponding memory operation (e.g., a program, read, or erase operation).

Each of the memory cells **100** can be programmed to store information representing a value of a single bit or a value of multiple bits such as two, three, four, or a higher number of bits. For example, each of the memory cells **100** can be programmed to store information representing a binary value "0" or "1" of a single bit. The single bit per cell is sometimes called a single level cell. In another example, each of the memory cells **100** can be programmed to store information representing a value representing multiple bits, such as one of four possible values "00," "01," "10," and "11" of two bits, one of eight possible values "000," "001," "010," "011," "100," "101," "110," and "111" of three bits, or one of another set of values of multiple bits. A cell that has an ability to store multiple bits is sometimes referred to as a multi-level cell (or multi-state cell). Various operations on these types of cells are discussed in more detail, below.

The memory device **101** can receive a supply voltage, including supply voltage signals Vcc and Vss, on a first supply line **130** and a second supply line **132**, respectively. Supply voltage signal Vss can operate at a ground potential (e.g., having a value of approximately zero volts). Supply voltage signal Vcc can include an external voltage supplied to the memory device **101** from an external power source such as a battery or an alternating-current to direct-current (AC-DC) converter circuitry (not shown in FIG. **1**).

The circuitry **112** of the memory device **101** is further shown to include a select circuit **115** and an input/output (I/O) circuit **116**. The select circuit **115** can respond to signals SEL**1** through SELn to select signals on the first data lines **106** and the second data lines **113** that can represent the information read from or programmed into the memory cells **100**. The column decoder **108** can selectively activate the SEL**1** through SELn signals based on the A**0** through AX address signals on the address lines **109**. The select circuit **115** can select the signals on the first data lines **106** and the second data lines **113** to provide communication between the memory array **102** and the I/O circuit **116** during read and programming operations.

The memory device **101** can include a non-volatile memory device and the memory cells **100** can include non-volatile memory cells such that the memory cells **100** can retain information stored therein when power (e.g., Vcc, Vss, or both) is disconnected from the memory device **101**.

Each of the memory cells **100** can include a memory element having material, at least a portion of which can be programmed to change the resistance value of the material. Each of the memory cells **100** can have a state corresponding to a resistance value when each of the memory cells **100** is programmed in a programming operation. Different resistance values can thus represent different values of information programmed in each of the memory cells **100**. This type of memory element and its related resistance values are discussed in more detail, below.

The memory device **101** can perform a programming operation when it receives (e.g., from an external processor or a memory controller) a programming command and a value of information to be programmed into one or more selected

ones of the memory cells **100**. Based on the value of the information, the memory device **101** can program the selected memory cells to cause them to have appropriate resistance values to represent the values of the information stored therein.

One of ordinary skill in the art may recognize that the memory device **101** may include other components, at least some of which are discussed herein. However, several of these components are not necessarily shown in the figure, so as not to obscure the various embodiments described. The memory device **101** may include devices and memory cells, and operate using memory operations (e.g., programming and erase operations) similar to or identical to those described below with reference to various other figures and embodiments discussed herein.

With reference now to FIG. **2**, a partial block diagram of a memory device **201** is shown to include a memory array **202** including memory cells **200** with access components **211** and memory elements **222**, according to an example embodiment. The memory array **202** may be similar or identical to the memory array **102** of FIG. **1**. As further shown in FIG. **2**, the memory cells **200** are shown to be arranged in a number of rows **230**, **231**, **232**, along with access lines, for example word lines, to conduct signals such as signals WL**0**, WL**1**, and WL**2**. The memory cells are also shown to be arranged in a number of columns **240**, **241**, **242** along with data/sense lines, for example bit lines, to conduct signals such as signals BL**0**, BL**1**, and BL**2**. The access components **211** can turn on (e.g., by using appropriate values of signals WL**0**, WL**1**, and WL**2**) to allow access to the memory elements **222** to read information from or program (e.g., write) information into the memory elements **222**.

Programming information into the memory elements **222** can include causing the memory elements **222** to have specific resistance values. Thus, reading information from the memory elements **222** can include measuring a resistance value of each of the memory elements **222**. Measuring the resistance can include sensing a value of a current flowing through various ones of the memory cells **200**. Based on a measured value of the current, a corresponding value of the information stored in the memory can be determined. A determination of the information based on the value of the current is discussed in more detail, below.

FIGS. **3** through **5** each show a schematic diagram of examples of different memory cells **300**, **400**, **500** having different access components **311**, **411**, **511** coupled to memory elements **333**, **444**, **555**, according to various embodiments. Lines labeled WL and BL in FIGS. **3** through **5** can correspond to any one of the access lines **104** and any one of the first data lines **106** of FIG. **1**, respectively. FIGS. **3** through **5** show examples of the access components **311**, **411**, **511** including a metal-oxide-semiconductor field-effect transistor (MOSFET), a bipolar junction transistor (BJT), and a diode, respectively. As will be realized by one of ordinary skill, upon reading this disclosure, the memory cells **300**, **400**, **500** can include other types of access components.

Each of the memory elements **333**, **444**, **555** can be coupled to and disposed between two electrodes, such as a first electrode **351** and a second electrode **352** (FIG. **3**), a first electrode **451** and a second electrode **452** (FIG. **4**), or a first electrode **551** and a second electrode **552** (FIG. **5**). FIGS. **3** through **5** schematically show each of these electrodes as dots. Structurally, each of these electrodes can include a conductive material. Respective ones of the memory elements **333**, **444**, **555** can include a material that can be changed, for example, in response to a signal, to have different resistance values. The value of information stored in the memory element can correspond to the resistance value of the memory element. The access components **311**, **411**, **511** can enable signals (e.g., embodied as a voltage or current) to be transferred to and from the memory elements **333**, **444**, **555** via the respective pairs of electrodes during operation of the memory cells such as read, program, or erase operations.

A programming operation may use signal WL to turn on the access components **311**, **411**, **511**, and then apply a signal (e.g., a signal having a programming voltage or current) through the memory elements **333**, **444**, **555**. Such a signal can cause at least a portion of the material of the memory elements **333**, **444**, **555** to change. The change can be reversed by, for instance, performing an erase operation. For example, dielectrics can be created at or near surfaces of one or more metals within the memory elements through oxidation of the one or more metals. The oxidation process is discussed in more detail, below, for example, with reference to FIGS. **6**A and **6**B. The dimensions of these dielectrics can be changed in at least a portion of the memory elements **333**, **444**, **555** during a programming operation. Different dimensions, such as different thicknesses, of the dielectric may cause the memory elements **333**, **444**, **555** to have different resistance values. The differences in resistance values can be used to represent different states that represent different values of the information that is stored in the memory elements **333**, **444**, **555**.

A read operation may use the signal WL to turn on the access components **311**, **411**, **511**, and then apply a signal having a voltage or a current (e.g., a read voltage or current) through the memory elements **333**, **444**, **555**. The read operation may measure the resistance of the memory cells **300**, **400**, **500**, based on a read voltage or current, to determine the corresponding value of information stored therein. For example, in each of the memory cells **300**, **400**, **500**, a different resistance value can impart a different value (e.g., voltage or current value) to signal BL when a read current passes through the memory elements **333**, **444**, **555**. Other circuitry of the memory device (e.g., a circuit such as the I/O circuit **116** of FIG. **1**) can use the signal BL to measure the resistance value of memory elements **333**, **444**, **555** to determine the value of the information stored therein.

The voltage or current used during a read, program, or erase operation can be different from one another. For example, in a programming operation, the value (e.g., the voltage) of the signal (e.g., the signal BL in FIG. **3** or FIG. **4** or the signal WL in FIG. **5**) that creates a current flowing through the memory element can be sufficient to cause the material of at least a portion of the memory element to change. The change can alter the resistance value of the memory element to reflect the value of the information to be stored in the memory elements **333**, **444**, **555**.

In a read operation, the value (e.g., the voltage) of the signal (e.g., the signal BL in FIG. **3** or FIG. **4** or the signal WL in FIG. **5**) that creates a current flowing through the memory element can be sufficient to create the current but insufficient to cause any portion of the memory element to change. Consequently, the value of the information stored in the memory element can remain unchanged during and after the read operation.

In an erase operation, the voltage value of the signal (e.g., the signal BL in FIG. **3** or FIG. **4** or the signal WL in FIG. **5**) can have an opposite polarity from the voltage used in a programming operation. The signal, creating a current in this case, can therefore change, or reset, the material of the memory element to its original state; for example, a state prior to any programming being performed on the memory cells.

Various ones or all of the memory cells **100**, **200**, **300**, **400**, **500** of FIGS. **1** through **5** can include a memory cell having a structure similar or identical to one or more of the memory cells described below.

For example, FIG. **6**A shows a cross-sectional view of a portion of a memory cell **600**, according to an example embodiment. The material in the memory cell **600** can have different states to store information representing a single bit or multiple bits, as described in more detail below with reference to FIGS. **7**A through **7**E and FIGS. **8**A through **8**D.

With continued reference to FIG. **6**A, the memory cell **600** is shown to include a top electrode **601**, a first dielectric **603**, a lower electrode **605**, a second dielectric **607**, a memory material **609**, and a multi-layer stack electrode **611** disposed between the top electrode **601** and the memory material **609**. In an example embodiment, the first dielectric **603** and the second dielectric **607** can each be fabricated from a variety of non-conductive materials including silicon dioxide (SiO_2), various types of silicon nitride (Si_xN_y), or other types of one or more dielectric materials known independently in the art. In other embodiments, the first dielectric **603** and the second dielectric **607** can be fabricated as a single continuous layer or as a series of layers. Details of exemplary fabrication processes are discussed in more detail, below, with reference to FIGS. **9**A through **9**F.

The top electrode **601** and the lower electrode **605** may each be fabricated from a number of conductive materials known in the art, and each electrode may be fabricated from the same material or from a different material. For example, the top electrode **601** and the lower electrode **605** can be fabricated from platinum (Pt), aluminum (Al), copper (Cu), tungsten (W), or a number of other conductive materials known independently in the art. The material chosen to fabricate the top electrode **601** and the lower electrode **605** can be an inert material, such that it may remain unchanged (e.g., the lower electrode **605** does not react with the memory material **609**) when a signal is applied to the top electrode **601** (e.g., during programming of the memory cell **600**). The top electrode **601** and the lower electrode **605** can each be deposited, sputtered, or otherwise formed onto a base material or substrate (not shown explicitly in FIG. **6**A but discussed with reference to FIGS. **9**A through **9**F, below). As used herein, the term substrate is simply chosen to refer to any of various substrate types used in the semiconductor and allied industries. Substrate types may therefore include silicon wafers, compound wafers, thin film head assemblies, polyethyleneterephthalate (PET) films, photomask blanks and reticles, or numerous other types of substrates known independently in the art.

The memory material **609** may be comprised of a dielectric material, which may include a combination of materials, including oxygen. For example, the memory material **609** can include $Pr_xCa_yMn_zO$, $La_xCa_yMnO_z$, $La_xSr_yCo_xY$, TiO_x, HfO_x, ZrO_x, and other dielectric materials.

The multi-layer stack electrode **611** can be comprised of a number of different metals. The metals can include, for example, aluminum (Al), platinum (Pt), titanium (Ti), tungsten (W), titanium nitride (TiN), tantalum nitride (TaN), tungsten nitride (WN_x), tungsten oxide (WO_x), ruthenium (Ru), ruthenium oxide (RuO_x), hafnium silicide ($HfSi_x$), nickel silicide ($NiSi_x$), and other metals or materials. Each of a first metal **611**A, a second metal **611**B, and a third metal **611**C of the multi-layer stack electrode **611** may include only a single element (e.g., only a single metal). For example, the first metal **611**A may include only a single metal (e.g., only aluminum), the second metal **611**B may include only a single metal (e.g., titanium) that is different from the metal of first metal **611**A, and the third metal **611**C may include only a single metal (e.g., tungsten) that is different from either the first **611**A or the second **611**B metals. Alternatively, one or more of the first **611**A, second **611**B, or third **611**C metals can include only a single element (e.g., only a single metal) and the remaining metal or metals can include a combination (e.g., a compound) of two or more elements. Moreover, each of the **611**A, second **611**B, and third **611**C metals can include a combination of two or more elements. For example, the first metal **611**A can include a combination of two or more elements and the second **611**B and third **611**C metals can each include other combinations of two or more elements where the combinations are each different from one another. In other embodiments, alternating metals or metal combinations (e.g., the first metal **611**A and the third metal **611**C) can be the same as one another but different from the second metal **611**B.

Although FIG. **6**A shows that the multi-layer stack electrode **611** includes the first **611**A, second **611**B, and third **611**C metals, the multi-layer stack electrode **611** can incorporate any number of metals. Thus, the three-metal stack shown in FIG. **6**A is merely provided as an example. Each of the metals in the multi-layer stack electrode **611** may be deposited or otherwise formed by, for example, atomic layer deposition (ALD), chemical vapor deposition (CVD), physical vapor deposition (PVD), or a number of other techniques and formation processes know independently in the semiconductor and related industries. In one embodiment, each of the metals in the multi-layer stack electrode **611** is deposited by ALD to a few monolayers in thickness. The ALD process allows a single monolayer of material to be formed at a time.

Each of the first **611**A, second **611**B, and third **611**C metals may physically contact each other, but they may or may not chemically bond to one another. For example, the first **611**A, second **611**B, and third **611**C metals of the multi-layer stack electrode **611** may not be, either partially or fully, bonded to one another as an alloy or compound. As shown with reference to FIG. **6**A, the third metal **611**C is electrically coupled to and can be at least partially in physical contact with the memory material **609**. The first metal **611**A is electrically coupled to and can be at least partially in physical contact with the top electrode **601**.

These direct contacts allow each of the first **611**A, second **611**B, and third **611**C metals to react with the memory material **609** during an operation (e.g., a program, read, or erase operation) of the memory cell **600**, perhaps allowing the memory cell **600** to have different states. For example, a positive voltage applied to the top electrode **601** may induce oxidation of the metal near an interface of one or more layers of the multi-layer stack electrode **611** and the memory material **609**. A large Gibbs free energy of oxidation results in a higher driving force towards oxide formation. The oxidation results in a resistive oxide layer that dominates an overall resistance of the memory cell **600** (as measured from the top electrode **601** to the lower electrode **605**), thereby switching the memory cell **600** into a more resistive state. As discussed below, the oxidation process is reversible. The resistive states can be used to represent different values of information stored in the memory cell **600**. A more detailed description of the various states is provided, below, with reference to FIGS. **7**A through **7**E and FIGS. **8**A through **8**D.

With reference now to FIG. **6**B, an alternative cross-sectional view of a portion of a memory cell **630** is shown, according to an example embodiment. Similar to the memory cell **600** of FIG. **6**A, the material in the memory cell **630** can have different states to store information representing a single bit or multiple bits. However, rather than the multi-layer stack electrode **611** construction of the memory cell **600** of FIG.

6A, the memory cell **630** of FIG. **6**B is shown to include a mixed layer electrode **631**. As described in more detail, below, the mixed layer electrode **631** of FIG. **6**B functions in a manner similar or identical to the multi-layer stack electrode **611** of FIG. **6**A. Although the mixed layer electrode **631** is shown to include a first **631**A, a second **631**B, and a third **631**C metal particle type, any number of particle types may be used.

The mixed layer electrode **631** of FIG. **6**B is comprised of a number of different metal particles. In an embodiment, the metal particles may be in physical contact with one another. In other embodiments, the metal particles may be isolated from one another by an intervening dielectric material formed between at least some of the metal particles; that is, a colloidal system (i.e., dispersed phase metal particles in a dielectric continuous medium). In other embodiments, the metal particles are randomly dispersed in the colloidal system. In still other embodiments, a combination of metal particles in contact with one another and the colloidal system may be used.

As with the multi-layer stack electrode **611** of FIG. **6**A, the mixed layer electrode **631** can include metal particles selected from a plurality of metals. For example, the metals can include aluminum (Al), platinum (Pt), titanium (Ti), tungsten (W), titanium nitride (TiN), tantalum nitride (TaN), tungsten nitride (WN_x), tungsten oxide (WO_x), ruthenium (Ru), ruthenium oxide (RuO_x), hafnium silicide ($HfSi_x$), nickel silicide ($NiSi_x$), and other metals or materials. Each of the first **631**A, second **631**B, and third **631**C metal particle type of the mixed layer electrode **631** may include only a single element (e.g., only a single metal). For example, the first metal particle type **631**A may include only a single metal (e.g., only aluminum), the second metal particle type **631**B may include only a single metal (e.g., titanium) that is different from the metal of first metal particle type **631**A, and the third metal particle type **631**C may include only a single metal (e.g., tungsten) that is different from either the first **631**A or the second **631**B metal particle types. Alternatively, one or more of the first **631**A, second **631**B, or third **631**C metal particle types can include only a single element (e.g., only a single metal) and the remaining particle or particles can include a combination (e.g., a compound) of two or more elements. Moreover, each of the **631**A, second **631**B, and third **631**C metal particle type can include a combination of two or more elements. For example, the first metal particle type **631**A can include a combination of two or more elements and the second **631**B and third **631**C metal particle types can each include other combinations of two or more elements that are each different from one another. In other embodiments, alternating metals or metal combinations (e.g., the first metal particle type **631**A and the third metal particle type **631**C) can be the same as one another but different from the second metal particle type **631**B.

FIGS. **7**A through **7**E show a memory cell **700** having various states and resistivity values, according to an example embodiment. The memory cell **700** is similar to the memory cell **600** of FIG. **6**A or the memory cell **630** of FIG. **6**B except for the number of metal layers within a two-layer stack electrode **711** as shown in FIGS. **7**A through **7**E. The two-layer stack electrode **711** has a first metal **713**A and a second metal **715**A. The first **713**A and the second **715**A metals can be formed similarly and from similar or the same materials as the first **611**A, second **611**B, and third **611**C metals of FIG. **6**A.

Thus, the two-layer stack electrode **711** has only two metals as compared with the three metals of the multi-layer stack electrode **611** or the three metal particle types of the mixed layer electrode **631** of FIG. **6**B. The practical difference between the two examples is the number of available states, which depends on the number of metal types. For example, in some embodiments, two metal types can yield four states (i.e., $2^2=4$), three metal types can yield eight states (i.e., $2^3=8$), four metal types can yield sixteen states (i.e., $2^4=16$), and so on. Thus, the two-layer stack electrode **711** is described for reasons of brevity. Upon reading this disclosure, one of ordinary skill in the art will understand how to apply the techniques described to more than two metal types, to construct and operate a memory cell with more than four corresponding available states.

With continuing reference to FIG. **7**A, under a certain condition, such as under the application of a signal in the form of a bias voltage (discussed with reference to FIGS. **7**B through **7**E) applied to the top electrode **601** during a programming operation performed on the memory cell **600**, the first **713**A and the second **715**A metals of the two-layer stack electrode **711** can react with the memory material **609**. As described below, the reaction between the materials can create a dielectric material from one or both of the first **713**A and the second **715**A metals and the memory material **609**. The presence or absence of the dielectric material or a change in the dimension (e.g., thickness) of the dielectric material can cause the memory cell **700** to have different memory states due to different resistance values caused by the presence/absence or various thicknesses of the one or more dielectric materials.

FIGS. **7**A through **7**D show four example states in the memory cell **700**, including state **0**, state **1**, state **2**, and state **3**. Each of these states can be created by applying different bias voltage levels to the top electrode **601** during a memory operation, such as a programming operation.

In FIG. **7**A, no bias voltage is applied (i.e., the bias voltage is approximately zero) and, consequently, no dielectric material is created in the memory material **609**. Thus, in this example, the memory cell **700** is at a state **0**.

In FIG. **7**B, and with continuing reference to FIG. **7**A, in response to applying a sufficient bias voltage V_1 (e.g., a sufficient magnitude of a positive voltage V_1) to the top electrode **601**, the two-layer stack electrode **711** can react with the memory material **609** to create a dielectric material **731**A having a thickness **731**B between the two-layer stack electrode **711** and the memory material **609**. The first metal **713**A or FIG. **7**A may be partially consumed to form a first metal **713**B and a portion of the dielectric material **731**A of FIG. **7**B. Thus, the dielectric material **731**A is at least partially an oxide of the first metal **713**B. The first metal **713**B is similar to the first metal **713**A but is partially consumed by an interaction with oxygen. The oxygen in the dielectric material **731**A is provided by the memory material **609**. For example, in response to the signal having a sufficient positive voltage (e.g., the bias voltage V_1), negative oxygen ions from the memory material **609** diffuse to the two-layer stack electrode **711** and react with the first metal **713**A of FIG. **7**A. The dielectric material **731**A therefore directly contacts the first metal **713**B.

As a result of the sufficient bias voltage V_1 being applied to the memory cell **700** at the top electrode **601**, the dielectric material **731**A in FIG. **7**B changes the structure of at least a portion of the memory material **609** relative to the structure shown in FIG. **7**A. Thus, the state of the memory cell **700** can also change, such as from state **0** (FIG. **7**A) to state **1** (FIG. **7**B) due to an increased resistance in the memory cell **700**. The increased resistance, as measured from the top electrode **601** to the lower electrode **605**, is due to the formation of the dielectric material **731**A.

With reference again to FIG. **7**A, the application of a sufficient bias voltage may create a dielectric material based on

only the first metal **713**A and not the second metal **715**A. The formation of any dielectric material is attributable to the first **713**A and the second **715**A metals being different from one another. Different materials (e.g., different metals) have different propensities to form oxide, based on, for example, the Gibb's free energy of oxide formation for each material. Thus, if the first metal **713**A (e.g., aluminum) is more reactive to oxide formation than the second metal **715**A (e.g., titanium), then for a given voltage (e.g., V_1) only a certain thickness of oxide may be generated. In this example, for the same bias voltage V_1, no oxide material (e.g., no oxide of titanium) may be created. However, if a voltage applied to the top electrode **601** is increased (e.g., to a voltage greater than V_1), then additional dielectric materials may also be created between portions of the second metal **715**A and the memory material **609**. In some embodiments, the potential of bias voltages for voltage V_1 include about 1 volt but can range from about 0 volts to about 5 volts.

Referring now to FIG. **7**C, in response to a sufficient bias voltage V_2 (e.g., a positive bias voltage V_2 greater than the bias voltage V**1** of FIG. 7B) applied to the top electrode **601**, the second metal **715**B of the two-layer stack electrode **711** may react with the memory material **609** to create a second dielectric material **753**A. The second dielectric material **753**A has a second thickness **753**B. Additionally, a first dielectric material **751**A has a first thickness **751**B greater than the thickness **731**B of the dielectric material **731**A of the memory cell **700** of FIG. **7**B. The dielectric material **731**A was formed by application of the bias voltage V_1. Thus, in response to the sufficient bias voltage V_2, negative oxygen ions from the memory material **609** diffused to the two-layer stack electrode **711** and reacted with the first **713**C and second **715**B metals. The reaction created oxide of material comprising the first **751**A and second **753**A dielectric materials. In some embodiments, the potential of bias voltages for voltage V_2 include about 1.4 volts but can range from about 0 volts to about 5 volts.

The additional thickness on the first dielectric material **751**A is due to more oxygen ions being attracted to the increased potential of V_2 over V_1, caused by the application of the bias voltage V_2 in FIG. **7**C. However, in some situations, depending at least partially on a composition of the memory material **609**, the application of the bias voltage V_1 of FIG. **7**B may saturate the oxidation mechanism for forming the dielectric material **731**A. When the oxidation mechanism is saturated, the application of an increased bias potential, for example, bias voltage V_2 of FIG. **7**C to the top electrode **601**, may cause the first thickness **751**B of the first dielectric material **751**A to be close to or substantially the same thickness as the thickness **731**B of the dielectric material **731**A of FIG. **7**B.

The formation of the first **751**A and the second **753**A dielectric materials of FIG. **7**C change the structure of the memory material **609** relative to the structures of the memory cell **700** shown in either FIG. **7**A or FIG. **7**B. Thus, the state of memory cell **700** can also change, such as from state **1** (FIG. 7B) to state **2** (FIG. 7C) due to an increased resistance in the memory cell **700**. The increased resistance, as measured from the top electrode **601** to the lower electrode **605**, is due to the formation of the first **751**A and the second **753**A dielectric materials.

In FIG. **7**D, in response to a sufficient bias voltage V**3** (e.g., a positive bias voltage V_3 greater than the bias voltage V_2 of FIG. 7C) applied to the top electrode **601**, the second metal **715**C of the two-layer stack electrode **711** may react with the memory material **609** to create a second dielectric material **773**A. The second dielectric material **773**A has a second thickness **773**B. Additionally, a first dielectric material **771**A has a first thickness **771**B greater than the first thickness **751**B of the first dielectric material **751**A of the memory cell **700** of FIG. **7**C. The first dielectric material **751**A (FIG. **7**C) was formed by application of the bias voltage V_2. Thus, in response to the sufficient bias voltage V_3, negative oxygen ions from the memory material **609** diffused to the two-layer stack electrode **711** and reacted with the first **713**D and the second **715**C metals. The reaction created oxides of material comprising the first **771**A and second **773**A dielectric materials. In some embodiments, the potential of bias voltages for voltage V_3 include about 1.4 volts but can range from about 0 volts to about 5 volts.

The additional thickness on the first dielectric material **771**A is due to more oxygen ions being attracted to the increased potential of V_3 over V_2 caused by the application of the bias voltage V_3 in FIG. **7**D. However, in some situations, depending at least partially on a composition of the memory material **609**, the application of the bias voltage V_1 of FIG. **7**B or V_2 of FIG. **7**C may saturate the oxidation mechanism for forming the dielectric material **731**A of FIG. **7**B or the first dielectric material **751**A of FIG. **7**C. When the oxidation mechanism is saturated, the application of an increased bias potential, for example, bias voltage V_3 of FIG. **7**D to the top electrode **601**, may cause the first thickness **771**B of first dielectric material **771**A to be close to or substantially the same thickness as the first thickness **751**B of the first dielectric material **751**A of FIG. **7**C.

The formation of the first **771**A and the second **773**A dielectric materials of FIG. **7**D change the structure of the memory material **609** relative to the structures of the memory cell **700** shown in any of FIG. **7**A, **7**B, or **7**C. Thus, the state of memory cell **700** can also change, such as from state **2** (FIG. 7C) to state **3** (FIG. 7D) due to an increased resistance in the memory cell **700**. The increased resistance, as measured from the top electrode **601** to the lower electrode **605**, is due to the formation of the first **771**A and the second **773**A dielectric materials.

As described, above, with reference to FIGS. **6**A and **6**B, the material of the lower electrode **605** can be an inert material. Thus, selecting the lower electrode to be formed from an inert material can prevent or reduce reactions between the lower electrode **605** and the memory material **609** during application of a bias voltage to the top electrode **601**. Consequently, during the applications of the bias voltages V_1, V_2, or V_3 to the top electrode **601**, as shown in FIGS. **7**B through **7**D, respectively, no dielectric materials may be created at the interface between the lower electrode **605** and the memory material **609**. Therefore, the lower electrode **605** can remain directly contacting the memory material **609** without a necessity for a dielectric material between the lower electrode **605** and the memory material **609**.

The application of the signals in the form of bias voltages V_1, V_2, or V_3 to create various ones of the dielectric materials between the interface of the multi-layer stack electrode **611** or the mixed layer electrode **631**, of FIGS. **6**A and **6**B, respectively, and the memory material **609**, as described above with reference to FIGS. **7**A through **7**D, can be applied during a programming operation. Although FIGS. **7**A through **7**D are only described in detail with reference to the multi-layer stack electrode **611**, one of ordinary skill in the art, upon reading this disclosure, will understand how the same or similar techniques are applicable with reference to the mixed layer electrode **631** of FIG. **6**B.

With reference now to FIG. **7**E, a signal in the form of a bias voltage V_4 with a polarity that is opposite to that of V_1, V_2, or V_3 (e.g., negative) is applied to the top electrode **601**. A sufficient negative bias voltage V_4 can reduce the thickness of

some or all of dielectric materials previously formed with reference to FIGS. 7B through 7D. Thus, the application of the negative bias voltage V_4 can be applied to the top electrode **601** during an erase operation. In response to the sufficiently negative bias voltage V_4 being applied to the top electrode **601**, negative oxygen ions from the various dielectric materials may diffuse to the memory material **609**, thereby reducing the thickness of the dielectrics. If the negative voltage at the top electrode **601** is sufficiently large, the negative voltage may dissolve the dielectric materials. Consequently, the memory cell **700** may return to its original state (e.g., state **0**) once the dielectric materials are sufficiently reduced in thickness or dissolved. In some embodiments, the potential of bias voltages for voltage V_4 include about 2 volts to full erase

For example, if the memory cell **700** is in any of state **1** (FIG. 7B), state **2** (FIG. 7C), or state **3** (FIG. 7D), the application of the bias voltage V_4 (e.g., with a polarity that is opposite to that of V_1, V_2, or V_3 and thus, sufficiently negative) to the top electrode **601** can reduce the thickness of or dissolve the formed dielectric materials between the top electrode **601** and the memory material **609** in these states. In this example, the memory cell **700** can return from state **1**, state **2**, or state **3** back to state **0** as shown in FIG. 7E. State **0** of FIG. 7E is the same state of the memory cell **700** of FIG. 7A, where substantially no dielectric materials are present in the memory material **609**.

As described above, the various states, such as states **0**, **1**, **2**, and **3** of the memory cell **700**, can each be used to represent information stored in the memory cell **700**. For example, the memory cell **700** can be used as a non-volatile two-bit memory cell. States **0**, **1**, **2**, and **3**, as described above, can be used to represent four possible combinations of the two bits.

Also as described above, the embodiments depicted in FIGS. 7A through 7D show the formation of four states **0**, **1**, **2**, and **3** of the memory cell **700**. However, any other number of states can be formed, by applying different signals having different voltage values to create different states. For examples, if the two-layer stack electrode had been fabricated with three rather than two metals, eight signals (or a single signal) having eight different voltages can be applied to the top electrode **601** to create eight corresponding different states in the memory cell **700**. The eight different states can be used to represent eight different possible combinations of three bits. In this example, the memory cell **700** can be used as a non-volatile three-bit memory cell.

The state of the memory cell **700**, such as states **0**, **1**, **2**, and **3**, can be formed during the programming of the memory device (e.g., the memory device **101** of FIG. **1**) in which the memory cell **700** resides. The information stored therein can then be retrieved during a read operation.

FIGS. **8**A through **8**D show the memory cell **700** of FIGS. 7A through 7D, respectively, having different values of currents i_0, i_1, i_2, and i_3 flowing from the top electrode **601** to the lower electrode **605** in various read operations. The current is produced in response to a signal having a voltage V_{read} being applied to the top electrode **601**, according to an example embodiment. The application of the signal having voltage V_{read} can be applied to the multi-layer stack electrode **611** during, for example, a read operation.

As shown in FIGS. **8**A through **8**D, the memory material **609** has zero or more dielectric materials, the dielectric materials having different thicknesses as noted with reference to FIGS. **7**A through **7**D. As a result of the different dielectric materials, the memory cell **700** can have different resistance values in each of FIGS. **8**A through **8**D.

For example, based on the thickness of the various dielectric materials, the resistance value in state **0** is less than the resistance value in state **1**; the resistance value in state **1** is less than the resistance value in state **2**; and the resistance value in state **2** is less than the resistance value in state **3**. As a result, the resistance value of the memory cell **700** is different in different states. Since the value of current through the memory cell **700** is inversely proportional to the differing resistances value of the memory cell **700** in the various states, each of the currents i_0, i_1, i_2, and i_3 have different values. Thus, i_1 is less than i_0, i_2 is less than i_1, and i_3 is less than i_2.

The value of V_{read} can be selected to be sufficient to create measurable currents i_0, i_1, i_2, and i_3, but insufficient to cause any portion of the memory material **609** to change. For example, the value of voltage V_{read} can be selected such that the thicknesses of the various dielectric materials remain unchanged. Consequently, the information stored in the memory cell **700** can remain unchanged during and after the read operation.

FIGS. **9**A through **9**F show various parts of a fabrication process to form a memory cell, according to an example embodiment. In FIG. **9**A, a dielectric material **903**A is deposited, thermally grown, sputtered or otherwise formed on a substrate **901**. The substrate **901** can include, for example, any of various substrate types used in the semiconductor and allied industries. Substrate types may therefore include silicon wafers, compound wafers, thin film head assemblies, polyethylene-terephthalate (PET) films, photomask blanks and reticles, or numerous other types of substrates known independently in the art.

The dielectric material **903**A can include, for example, silicon dioxide (SiO_2), silicon nitride (Si_3N_4), or a number of other types of dielectric material or materials independently known to a skilled artisan. In other embodiments, the dielectric material **903**A may consist of several dielectric layers.

In FIG. **9**B, the dielectric material **903**A of FIG. **9**A has been etched or otherwise partially opened thus forming an opened dielectric **903**B. An aperture **905** in the opened dielectric **903**B can take on a number of geometries. For example, in one embodiment, the aperture has a circular shape (as seen from a plan-view—not shown). In another embodiment, the aperture **905** may comprise a trench having substantially parallel sides.

In FIG. **9**C, the aperture **905** is at least partially filled with an electrode material **906**. The electrode material **906** can be comprised of any of the materials described, above, with reference to the lower electrode **605** or the top electrode **601** of FIGS. **6**A and **6**B.

In an embodiment, the electrode material **906** can completely fill the aperture **905**. In this embodiment, the electrode material **906** may then be planarized (by, for example, chemical mechanical planarization (CMP)) to be substantially coplanar with an upper surface of the opened dielectric **903**B. In this embodiment, an additional opened dielectric **904** may subsequently be formed above the opened dielectric **903**B and the upper surface of the electrode material **906**.

In an alternative embodiment, the electrode material **906** only partially fills the aperture **905**. In this embodiment, a remaining, unfilled portion of the aperture **905** is used in subsequent fabrication process activities.

In other embodiments, the substrate **901** may instead be comprised of one or more materials similar to the lower electrode **605** or the top electrode **601** of FIGS. **6**A and **6**B. In this embodiment, the process activities associated with FIG. **9**C are optional as the electrode material **906** is already formed (i.e., as the substrate **901**).

In FIG. **9**D, the aperture **905** is at least partially filled with a memory material **907**. The memory material **907** can be comprised of any of the materials described, above, for the memory material **609**.

In an embodiment, the memory material **907** can fill any remaining portion of the aperture **905** left unfilled by the electrode material **906**. In this embodiment, the memory material **907** may then be planarized (by, for example, chemical mechanical planarization (CMP)) to be substantially co-planar with an upper surface of the opened dielectric **903**B. In this embodiment, another opened dielectric **908** may then be formed above the opened dielectric **903**B and the upper surface of the memory material **907**.

In an alternative embodiment, the memory material **907** only partially fills the aperture **905**. In this embodiment, a remaining portion of the aperture **905** is used in subsequent fabrication process activities.

With reference to FIG. **9**E, a multi-metal electrode **909** is formed above the memory material **907**. The multi-metal electrode **909** can be formed either within the newly formed aperture formed above the opened dielectric **903**B and the upper surface of the memory material **907**, or within any remaining portion of the aperture **905**.

In an embodiment, the multi-metal electrode **909** is fabricated by two or more sequential depositions or other formation techniques of two or more metals. This embodiment of a fabrication method may be used to fabricate a portion of a memory cell similar to the memory cell **600** of FIG. **6**A. Various techniques, for example, ALD, have already been described above with reference to FIG. **6**A.

In an alternative embodiment, the multi-metal electrode **909** is fabricated by depositing or otherwise forming two or more metals substantially concurrently. This embodiment of a fabrication method may be used to fabricate a portion of a memory cell similar to the memory cell **630** of FIG. **6**B.

Regardless of which fabrication method is chosen, the multi-metal electrode **909** may comprise any of the materials described, above, with reference to the multi-layer stack electrode **611** of FIG. **6**A or the mixed layer electrode **631** of FIG. **6**B. After formation of the multi-metal electrode **909**, an annealing operation may be used to at least partially oxidize one or more of the metals in the multi-metal electrode **909**. In one embodiment, the oxygen atoms to oxidize the one or more of the metals in the multi-metal electrode **909** are supplied by the memory material **907**. In another embodiment, the oxygen atoms to oxidize the one or more of the metals in the multi-metal electrode **909** are supplied by gaseous oxygen introduced as part of the fabrication process. In still another embodiment, the oxygen atoms to oxidize the one or more of the metals in the multi-metal electrode **909** are supplied by a combination of the memory material **907** and the gaseous oxygen. An optional CMP operation may be used after fabricating the multi-metal electrode **909** to form a substantially co-planar upper surface of the multi-metal electrode **909** and the opened dielectric **903**B.

In FIG. **9**F, a top electrode **911** is deposited, sputtered, or otherwise formed above the upper surface of the multi-metal electrode **909** and the opened dielectric **903**B. Although shown as completely covering the upper surface of the multi-metal electrode **909** and the opened dielectric **903**B, the top electrode **911** in some embodiments does not do so, being applied only to a degree sufficient to enable electrical communication with the multi-metal electrode **909**. The top electrode may be comprised of any of the materials discussed, above, with reference to the top electrode **601** of FIGS. **6**A and **6**B.

Although the fabrication process in FIGS. **9**A through **9**F is shown to include only two metal components in the multi-metal electrode **909**, one of ordinary skill in the art, upon reading this disclosure, will appreciate that any number of metals or components can be employed. Further, each of the metals may vary in thickness relative to the one or more additional metals. In the case of the metal components being formed substantially concurrently, the ratio of one of the metal components to the other metal components may be similar or may vary considerably, one to another, and may be held relatively constant in some embodiments.

The various illustrations of apparatus (e.g., the memory device **101** and various ones of the memory cell **600**, **630**, **700**) are intended to provide a general understanding of the structure of various embodiments and are not intended to provide a complete description of all the elements and features of the apparatus that might make use of the structures, feature, and materials described herein.

The apparatus of the various embodiments may include or be included in, for example, electronic circuitry used in high-speed computers, communication and signal processing circuitry, single or multi-processor modules, single or multiple embedded processors, multi-core processors, data switches, and application-specific modules including multilayer, multi-chip modules, or the like. Such apparatus may further be included as sub-components within a variety of electronic systems, such as televisions, cellular telephones, personal computers (e.g., laptop computers, desktop computers, hand-held computers, tablet computers, etc.), workstations, radios, video players, audio players, vehicles, medical devices (e.g., heart monitors, blood pressure monitors, etc.), set top boxes, and various other electronic systems.

The various embodiments described herein include a memory device and methods of forming the same. The memory device can include an electrode coupled to a memory element. The electrode can include different materials forming different portions of the electrode. These materials can create different dielectric materials contacting the memory elements at different locations. Various states of the materials in the memory device can be used to represent stored information. Other embodiments are described above with reference to the various figures.

The above description and the drawings illustrate some embodiments of the invention to enable those skilled in the art to practice the embodiments of the invention. Other embodiments may incorporate structural, logical, electrical, process, or other changes. Examples merely typify possible variations. Portions and features of some embodiments may be included in, or substituted for, those of others. Many other embodiments will be apparent to those of ordinary skill in the art upon reading and understanding the description provided herein.

The Abstract of the Disclosure is provided to comply with 37 C.F.R. §1.72(b), requiring an abstract that allows the reader to quickly ascertain the nature of the technical disclosure. It is submitted with the understanding that it will not be used to interpret or limit the claims. In addition, in the foregoing Detailed Description, it may be seen that various features are grouped together in a single embodiment for the purpose of streamlining the disclosure. This method of disclosure is not to be interpreted as limiting the claims. Thus, the following claims are hereby incorporated into the Detailed Description, with each claim standing on its own as a separate embodiment.

What is claimed is:

1. A memory device comprising:

at least one memory element to store information; and

a first electrode coupled to the at least one memory element, the first electrode having a plurality of metals, the plurality of metals being dispersed substantially randomly over a surface of the at least one memory element coupled to the plurality of metals, a first metal of the plurality of metals having a Gibbs free energy of oxidation lower than a Gibbs free energy of oxidation of a second metal of the plurality of metals.

2. The memory device of claim **1**, wherein each of the plurality of metals is layered and substantially parallel to a surface of the at least one memory element coupled to the plurality of metals.

3. The memory device of claim **1**, wherein the at least one memory element is configured to store multiple bits of information.

4. The memory device of claim **1**, further including a second electrode coupled to the at least one memory element such that the at least one memory element is disposed between the second electrode and the first electrode.

5. The memory device of claim **1**, wherein the at least one memory element includes at least one of $Pr_xCa_yMn_zO$, $La_xCa_yMnO_z$, $La_xSr_yCo_xY$, TiO_x, HfO_x, or ZrO_x.

6. The memory device of claim **1**, wherein the at least one memory element includes a mixed valence oxide.

7. A memory device comprising:

a plurality of metals, a first metal of the plurality of metals having a Gibbs free energy of oxidation lower than a Gibbs free energy of oxidation of a second metal of the plurality of metals; and

a memory element coupled to the plurality of metals, the memory element to provide oxygen atoms to the plurality of metals when a bias voltage is applied across the memory element and the plurality of metals, the memory element being at least partially comprised of a mixed valence oxide.

8. The memory device of claim **7**, wherein the Gibbs free energy of oxidation of the first metal of the plurality of metals is more negative than a Gibbs free energy of oxidation of the memory element.

9. The memory device of claim **7**, further comprising a first electrode and a second electrode, the plurality of metals and the memory element being disposed between the first electrode and the second electrode.

10. The memory device of claim **7**, wherein the memory element is configured to store bits of information.

11. The memory device of claim **8**, wherein the memory element includes oxygen.

12. A memory device comprising:

a first electrode to be coupled to a first voltage supply terminal;

at least one memory element coupled to the first electrode and comprising a mixed valence oxide; and

a second electrode to be coupled to a second voltage supply terminal, the second electrode including a plurality of metals coupled to the at least one memory element, the plurality of metals having at least one metal oxide to store information in the at least one memory element in response to an electrical bias generated by a voltage supply, when the voltage supply is coupled to the first and the second electrodes.

13. The memory device of claim **12**, wherein a first metal of the plurality of metals has a Gibbs free energy of oxidation lower than a Gibbs free energy of oxidation of a second metal of the plurality of metals.

14. The memory device of claim **12**, wherein the at least one memory element includes a material having oxygen.

15. A method of forming a memory device, the method comprising:

forming a memory material;

forming a first metal over the memory material, the first metal having a Gibbs free energy of oxidation more negative than a Gibbs free energy of the memory material;

forming a second metal over the memory material, the second metal having a Gibbs free energy of oxidation more negative than the Gibbs free energy of oxidation of the first metal; and

annealing the memory device to at least partially oxidize the first metal and the second metal.

16. The method of claim **15**, further comprising supplying oxygen atoms to oxidize the first metal and the second metal by the memory material.

17. The method of claim **15**, further comprising supplying gaseous oxygen to the memory device during the annealing to supply oxygen atoms to oxidize the first metal and the second metal.

18. The method of claim **15**, further comprising forming the first metal and the second metal in alternate layers.

19. The method of claim **15**, further comprising forming the first metal and the second metal concurrently.

20. A method of forming a memory device, the method comprising:

forming a mixed valence oxide;

forming a first metal over the mixed valence oxide;

forming a second metal over the mixed valence oxide; and

at least partially oxidizing the first metal and the second metal with oxygen atoms from the mixed valence oxide.

21. The method of claim **20**, wherein forming the first metal and the second metal over the mixed valence oxide further comprise:

forming the first metal having a Gibbs free energy of oxidation more negative than a Gibbs free energy of oxidation of the mixed valence oxide; and

forming the second metal having a Gibbs free energy of oxidation more negative than the Gibbs free energy of oxidation of the first metal.

22. The method of claim **20**, further comprising forming the first metal and the second metal consecutively.

23. The method of claim **20**, further comprising forming the first metal and the second metal concurrently.

24. The method of claim **20**, wherein the first metal and the second metal include different metal materials.

25. A memory device comprising:

a plurality of metals, a first metal of the plurality of metals having a Gibbs free energy of oxidation lower than the Gibbs free energy of oxidation of a second metal of the plurality of metals; and

a memory element coupled to the plurality of metals, the plurality of metals being dispersed substantially randomly over a surface of the memory element coupled to the plurality of metals, the memory element to provide oxygen atoms to the plurality of metals when a bias voltage is applied across the memory element and the plurality of metals, the memory element being at least partially comprised of a mixed valence oxide.

26. A memory device comprising:

a first electrode to be coupled to a first voltage supply terminal;

at least one memory element coupled to the first electrode and comprising a mixed valence oxide; and

a second electrode to be coupled to a second voltage supply terminal, the second electrode including a plurality of metals coupled to the at least one memory element, the

plurality of metals being dispersed substantially randomly over a surface of the at least one memory element coupled to the plurality of metals, the plurality of metals having at least one metal oxide to store information in the at least one memory element in response to an electrical bias generated by a voltage supply, when the voltage supply is coupled to the first and the second electrodes.

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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 8,592,795 B2
APPLICATION NO. : 13/175320
DATED : November 26, 2013
INVENTOR(S) : Gurtej S. Sandhu et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the Claims

In column 17, line 47, In Claim 11, delete “claim 8,” and insert -- claim 7, --, therefor.

Signed and Sealed this
Twenty-fifth Day of March, 2014

Michelle K. Lee
Deputy Director of the United States Patent and Trademark Office